# THE NICKEL BULLETIN

A Monthly Summary of Recent Literature

MAY

1959 Volume 32 No. 5

THE MOND NICKEL COMPANY LIMITED
THAMES HOUSE MILLBANK LONDON SW1
Telephone: VICtoria 3888

# INDEX

## Mond Carbonyl Nickel Powder

*Page 137*


Page

**General**

Vacuum-Induction Melting 138
Electrical and Thermal Resistivity of Metals at Low Temperatures 138
Diffusion and Oxidation of Metals: Literature Reviews 138
Determination of Proof Stress of Steel at Elevated Temperatures 138
Analytical Chemistry in the Atomic Energy Field 138

**Nickel**

B.S. Specifications for Nickel and Nickel Alloys 139

**Electrodeposition and Other Coating Methods**

Metal-Finishing Processes: Institute of Metal Finishing Conference 140
Blackening of Nickel Anodes During Electrodeposition of Black Nickel 144
Effect of Purity of Water in Electroplating Solutions 144
Electroless Nickel Plating of Carbon 144
Co-Deposition of Tungsten and of Molybdenum with Nickel and Other Metals 145
Electrodeposited Nickel/Chromium Coatings: Influence of Thickness and Quality of Chromium 145
Corrosion-Resistance of Copper/Nickel/Chromium Electrodeposited Coatings 146
Influence of Nickel and Nickel-Chromium Underlayers on Adhesion of Evaporated Aluminium Films 147

**Non-Ferrous Alloys**

Nickel-Aluminium-Bronze Propellers: Production and Properties 148

**Nickel-Iron Alloys**

Properties of Magnetic-Amplifier Core Materials 148
Anisotropy and Magnetostriction Constants of Single Crystals of Nickel and Nickel-containing Alloys 149
Influence of High Temperature on Performance of 'Alnico V' and 'Alnico VI' Permanent Magnets 149

Page

**Cast Iron**

Purification of Cast Iron by Oxidation 150
Cast Irons for Die Blocks 150
Growth and Scaling Tests on Cast Irons 150

**Constructional Steels**

Determination of Cobalt in Nickel and Nickel-containing Steels 151
Cadmium Plating of High-Strength Steels 151

**Heat- and Corrosion-Resisting Materials**

The 'Nimonic' Alloys 151
Influence of Composition on High-Temperature Properties of Nickel-Molybdenum-Chromium-Iron Alloys 152
Compressive, Bearing and Shear Creep-Rupture Properties at Elevated Temperatures 153
Structure of Precipitation-Hardening Nickel-base High-Temperature Alloys 153
'Unitemp 212': Nickel-Chromium Precipitation-Hardenable Steel 155
Resistance of High-Temperature Materials to Attack by Boron Oxide 156
Oxidation of Chromium-Nickel Steels 157
Oxidation-Resistant Coatings for Molybdenum 158
Use of 'Inconel X' in High-Speed Research Aircraft 159
Influence of Heat-Treatment on Properties of Corrosion-Resisting Nickel-Molybdenum-Iron Alloys 159
Corrosion of Metals in Marine Tropical Atmospheres 160
Comparative Corrosion-Resistance of Chromium-Manganese-Nickel and Chromium-Nickel Austenitic Steels 161
Chloride Stress-Corrosion Cracking of Austenitic Steels: Hydrochloric-Acid Cleaning Solutions 162
Resistance of Nickel-bearing Materials to Nitric-Acid/Hydrofluoric-Acid Solutions containing Reducing Agents 163
Corrosion of Austenitic Steels in Acids: Evaluation by Three Methods of Test 163
Corrosion by Hydrogen Sulphide 164
Cathodic Protection in Chemical Plant 164
Design of Stainless-Steel Extrusions 165
Stainless-Steel Equipment in the Wet-Milling of Corn 165
Stainless Steel in Railway Engineering 165

**Analysis** 165

# MOND CARBONYL — NICKEL POWDERS

**Brief notes on properties and Applications**

## Grade A

This grade has a particle size of less than 10 microns; the particles are compact in nature, although granular rather than spherical. (See Fig. 1.)

The grade is generally used for conventional powder-metallurgy applications, for example, for production of special materials by sintering from mixtures of the component metals, e.g., small alloy-steel parts, magnets, nickel-iron alloys, heavy metals containing tungsten, silver-nickel contact materials, etc.

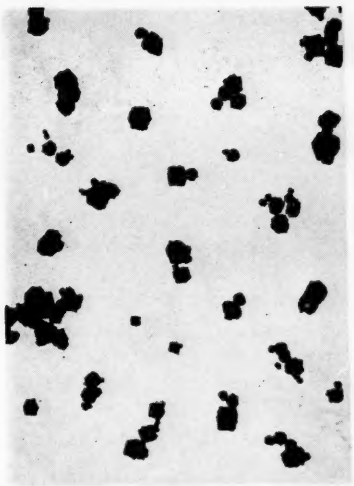

*Figure 1. Electron shadowgraph of Grade A nickel powder.*

## Grade B

The characteristic feature of this grade is its low bulk density, related to the peculiar particle characteristics, the powder being composed of chainlike structures of small cross section, as illustrated in Fig. 2. It is thus not possible to give a true figure for average particle-size calculation. Surface-area determination gives an equivalent mean particle size of the order of 2·5 microns.

The principal application of this type of powder is for the production of highly porous sintered bodies—in particular, nickel/cadmium battery plates. It also has some other uses in powder-metallurgy work where a very active powder, i.e., with a larger specific surface area than that of Grade A, is required. The bulk density can be increased by ball-milling, which causes the powder to lose its 'fluffy' nature.

*Figure 2. Electron shadowgraph of Grade B nickel powder.*

**Typical Chemical Analyses**

| | Grade A | Grade B |
|---|---|---|
| Carbon .. | less than 0·1% | less than 0·2% |
| Oxygen .. | „ „ 0·15% | „ „ 0·2% |
| Sulphur .. | „ „ 0·001% | „ „ 0·001% |
| Iron .. | „ „ 0·02% | „ „ 0·02% |
| Nickel .. | balance | balance |

All other elements absent, or present only in spectroscopic traces.

**Physical Characteristics**

| | Grade A | Grade B |
|---|---|---|
| Bulk density | 2·0-2·5 gm./cc. | 0·8-1·1 gm./cc. |
| Tapped density | 3·0-3·5 „ | — |
| Angle of repose* | 60°-65° | 65°-70° |

* Owing to the extreme fineness of all carbonyl powders, definition of flowability characteristics by methods used for other, coarser, powders is impracticable.

# ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

## GENERAL

### Vacuum-Induction Melting

F. N. DARMARA, J. S. HUNTINGTON and E. S. MACHLIN: 'Vacuum-Induction Melting.'

*Jnl. Iron and Steel Inst.*, 1959, vol. 191, Mar., pp. 266–75.

The paper falls into four sections. The first comprises a brief review of the history of vacuum-induction melting, the second describes the equipment required for large-scale operation, while in the third the authors discuss the basic principles which underlie the process. The last section, which outlines the uses of vacuum-induction melting, describes the advantages achieved by application of the process to the production of high-purity alloys, alloys containing reactive elements, and those requiring exceptionally close control of composition. Much of the information contained in the last section relates to high- and low-alloy nickel-containing materials.

### Electrical and Thermal Resistivity of Nickel at Low Temperatures

G. K. WHITE and S. B. WOODS: 'Electrical and Thermal Resistivity of the Transition Elements at Low Temperatures.'

*Philosophical Trans., Royal Soc., London, Ser. A*, 1959, vol. 251, Mar. 12, pp. 273–302.

The thermal resistivity ($W$) and electrical resistivity ($p$) of the following elements were measured over the range 2° to 140°K. (−271° to −133°C. and 2° to 300°K. (−271° to −27°C.), respectively: titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum. From the data so obtained the authors have deduced values for the 'ideal' resistivities $p_i$ and $W_i$ over the temperature ranges 295° to 10°K. (−22° to −263°C.) and 100° to 20°K. (−173° to −253°C.). The results are tabulated and discussed.

### Diffusion and Oxidation of Metals: Literature Reviews

*Industrial and Engineering Chemistry*, 1959, vol. 51, Mar., Pt. II contains the annual reviews of recent literature in fields of interest to chemists and chemical engineers. The scope of two reviews which include references to work on nickel and nickel-containing materials is shown in the right-hand column.

P. SHEWMON: 'Diffusion in Metals', pp. 402–5.

The review, which is supported by a *bibliography* of 106 items, is divided into sections on alloy diffusion, diffusion in pure metals, off-diagonal terms, diffusion in liquids, diffusion of interstitials, and diffusion along surfaces.

---

W. W. SMELTZER and L. H. EVERETT: 'Oxidation of Metals', pp. 406–11.

The literature is discussed in sections relating to review papers, theory of oxidation, properties of metal oxides, and oxidation behaviour of specific metals and alloys. The *bibliography* contains 196 references.

### Determination of Proof Stress of Steel at Elevated Temperatures

BRITISH STANDARDS INSTN.: 'Mechanical Testing of Steel at Elevated Temperatures. Part 1, Determination of Proof Stress.'

*B.S.* 3082: Part 1: 1959; 8 pp. Price 3/–.

The standard, which is one of a series dealing with mechanical testing of steel at elevated temperatures, has been drawn up to facilitate comparison of different steels and to unify the methods by which proof-stress data are obtained. It defines relevant terms and symbols and lays down requirements with respect to test-piece dimensions, determination of elongation, heating apparatus, measurement and control of temperature, rate of testing, measurement of load, and determination of proof stress.

### Analytical Chemistry in the Atomic Energy Field

R. W. BANE and J. K. BRODY: 'Analytical Chemistry in a Nuclear Research and Development Laboratory.'

*Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Paper A/15/P/954*, June, 1958; 25 pp.

A survey of some of the major work done by analytical groups working under the Manhattan project. An account is given of some of the unusual techniques which have been developed, and methods adopted for analysis of a wide range of materials employed in plant and fuels are outlined. Reference is made, *inter alia*, to analysis of a number of nickel-containing alloys, including Zr-U-Ni, Al-Ni-B, Zr-Sn-Cr-Fe-Ni ('Zircaloy').

The report includes a *bibliography* of 51 items, correlated with the text.

## NICKEL

### B.S. Specifications for Nickel and Nickel Alloys

The British Standards Institution has recently published a series of standards laying down revised requirements for nickel and nickel alloys, in cast and wrought forms, for use in general engineering applications. Each of the standards, which supersede those issued in 1949 as *B.S.* 1525-37, is divided into two sections: the first stipulates general requirements in relation to test specimens, testing, tolerances, inspection, etc.; the second lays down, for each of the materials covered, specific requirements with respect to mechanical and other relevant properties, composition limits, and the condition in which the material is to be supplied. The schedules are correlated below with the materials to which they relate and the standards which they replace.

'Nickel-Copper Alloy Castings.'
*B.S.* 3071 : 1959; 11 pp. Price 4/–.

*B.S.* 1537 referred to one alloy only. In the present standard two further alloys of higher silicon contents have been added, to meet Service requirements. Castings in the following materials are covered:

NA 1 Nickel-Copper (1 per cent silicon).
Copper 28–32, manganese 0·5–1·5, silicon 0·5–1·5, carbon 0·1–0·3, magnesium 0·08–0·12, iron 3 max., sulphur 0·05 max., lead 0·005 max., per cent., remainder nickel and cobalt.

NA 2 Nickel-Copper (2·75 per cent. silicon).
Composition as for NA 1 with the following modifications:
silicon 2·5–3, carbon 0·15 max., per cent.

NA 3 Nickel-Copper (4 per cent. silicon).
Composition as for NA 2 with the following modification: silicon 3·5–4·5.

---

'Nickel and Nickel Alloys: Sheet.'
*B.S.* 3072 : 1959; 20 pp. Price 5/–.

In the earlier series, the requirements for sheet and strip were included together in *B.S.* 1525-7. The requirements as amended, particularly with reference to tolerances, are not identical, and it has been decided to separate the two forms. *B.S.* 3072 now covers given thicknesses and sizes of sheet, in the cold-rolled-and-annealed and hot-rolled-and-annealed conditions, in the materials listed. Low-carbon nickel is included for the first time.

NA 11 Nickel*
NA 12 Low-Carbon Nickel †
NA 13 Nickel-Copper Alloy ‡
NA 14 Nickel-Chromium-Iron Alloy §

---

'Nickel and Nickel Alloys: Strip.'
*B.S.* 3073 : 1959; 18 pp. Price 5/–.

Covering requirements for strip, as amended from those contained in *B.S.* 1525-7 of the earlier series, which the present standard replaces. The schedule relates to given sizes of cold-rolled-and-annealed strip in the following materials:

NA 11 Nickel*
NA 13 Nickel-Copper Alloy‡
NA 14 Nickel-Chromium-Iron Alloy §

---

'Nickel and Nickel Alloys: Tube.'
*B.S.* 3074 : 1959; 19 pp. Price 5/–.

Replacing *B.S.* 1531-33 and covers cold-drawn and cold-drawn-and-annealed tube ($\frac{1}{4}$–$3\frac{3}{4}$ inches in outside diameter) in the materials listed. Low-carbon nickel is included for the first time.

NA 11 Nickel*
NA 12 Low-Carbon Nickel †
NA 13 Nickel-Copper Alloy ‡
NA 14 Nickel-Chromium-Iron Alloy §

---

'Nickel and Nickel Alloys: Wire.'
*B.S.* 3075 : 1959; 12 pp. Price 4/–.

Replacing *B.S.* 1534-36 and covering cold-drawn and cold-drawn-and-annealed wire (0·0048–0·3125 inch in diameter) in the materials noted below.

NA 11 Nickel*
NA 13 Nickel-Copper Alloy ‡
NA 14 Nickel-Chromium-Iron Alloy §

---

'Nickel and Nickel Alloys: Rods and Sections.'
*B.S.* 3076 : 1959; 19 pp. Price 5/–.

Covering hot-rolled and hot-rolled-and-annealed rods and sections, in given sizes, in the four materials listed. Three of the materials were included in *B.S.* 1528-30, but mechanical properties and chemical composition have been modified in the present standard. Low-carbon nickel is included for the first time.

NA 11 Nickel*
NA 12 Low-Carbon Nickel †
NA 13 Nickel-Copper Alloy ‡
NA 14 Nickel-Chromium-Iron-Alloy §

---

* Composition requirements of materials designated by the code number NA 11 are given as: nickel (including cobalt) 99 min., carbon 0·15 max., silicon 0·15 max., manganese 0·35 max., magnesium 0·2 max., titanium 0·1 max., per cent. Impurities: copper 0·25 max., iron 0·4 max., sulphur 0·01 max., per cent.

† Composition requirements of materials designated by the code number NA 12 are as for NA 11, with the following modification: carbon 0·02 max., per cent.

‡ Composition requirements of materials designated by the code number NA 13 are given as: nickel (including cobalt) 63 min., copper 28-34, carbon 0·3 max., silicon 0·5 max., iron 2·5 max., manganese 2 max., per cent. Impurities: aluminium 0·5 max., sulphur 0·02 max., per cent.

§ Composition requirements of materials designated by the code number NA 14 are given as: nickel (including cobalt) 72 min., chromium 14-17, iron 6-10, carbon 0·2 max., silicon 0·5 max., manganese 1 max., per cent. Impurities: copper 0·7 max., sulphur 0·03 max., per cent.

### Diffusion and Oxidation of Metals: Literature Reviews

See abstract on p. 138.

### Electrical and Thermal Resistivity of Nickel at Low Temperatures

See abstract on p. 138.

**Determination of Cobalt in Nickel**

See abstract on p. 151.

**Analytical Chemistry in the Atomic Energy Field**

See abstract on p. 138.

**Cathodic Protection in Chemical Plant**

See abstract on p. 164.

## ELECTRODEPOSITION AND OTHER COATING METHODS

### Metal-Finishing Processes: Institute of Metal Finishing Conference

The 1959 Annual Conference of the Institute of Metal Finishing was held at Brighton in April. The scope of the twenty-four papers presented during the five technical sessions is indicated in the abstracts below.

**Treatment of Aluminium**

J. M. KAPE and E. C. MILLS: 'The Production of Coloured Anodic Films Without the Use of Dye Stuffs', *Paper No.* 1.

Investigation of methods of obtaining coloured anodized aluminium by means of inorganic pigments and sealing treatments.

---

J. J. DALE, L. H. ESMORE and I. J. HOWELL: 'Making Mirrors by Bright Anodizing Pure Aluminium', *Paper No.* 2.

The paper gives details of investigations relating to the development of a mirror with an optically true surface capable of being bright anodized to give minimum susceptibility to scratches, pits, bloom and ripple.

---

**Deposition of Precious Metals**

F. H. REID: 'Some Experimental Observations on the Effect of Addition Agents on Stress and Cracking in Rhodium Deposits', *Paper No.* 3.

See *Trans. Inst. Metal Finishing*, 1959, vol. 36, Pt. III, pp. 74–81.

The paper is concerned primarily with the trend of recent developments towards the production of crack-free rhodium deposits. Addition of 1 g./L. of selenic acid to electrolytes containing 50 ml./L. of sulphuric acid results in deposits which, in relation to corrosion-resistance, may be regarded as virtually crack-free.

---

R. R. BENHAM: 'Some Observations on Silver Anodes', *Paper No.* 4.

See *Trans. Inst. Metal Finishing*, 1958, vol. 36, Pt. I, pp. 22–6.

Arising from troubles experienced with the shedding or flaking of silver anodes, a series of investigations was carried out to determine the effects, on the behaviour and appearance of the anodes, of grain size, anode current density and the presence of impurities.

---

R. N. RHODA: 'Electroless Palladium Plating', *Paper No.* 5.

See *Trans. Inst. Metal Finishing*, 1959, vol. 36, Pt. III, pp. 82–5.

The author describes a process for deposition of palladium by chemical reduction on catalytic surfaces.

---

R. H. ATKINSON: 'Electrodeposition of Platinum from Chloroplatinic Acid', *Paper No.* 6.

See *Trans. Inst. Metal Finishing*, 1958, vol. 36, Pt.I, pp. 7–16.

The experiments described were carried out to determine optimum conditions for production of ductile deposits.

---

**Nickel Plating**

J. EDWARDS: 'The Properties of Bright-Nickel Electrodeposits in Relation to the Period of Service of the Plating Bath: III. Composition and Microstructure', *Paper No.* 7.

See *Trans. Inst. Metal Finishing*, 1959, vol. 36, Pt. III, pp. 85–92.

The paper is the third reporting the results of research to obtain reliable information on the influence of long service of bright-nickel-plating solutions on the physical and mechanical properties of the resultant electrodeposits, and to estimate the extent of deterioration which might be caused by undue prolongation of use. Two proprietary bright-nickel solutions were selected for study: 'Super Gleamax' and 'Efco-Udylite No. 31'. The first and second parts of the report were published in *Trans. Inst. Metal Finishing*, 1958, vol. 35, *Advance Copy No.* 3 (see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 6, p. 161); Part 1 related to the physical and mechanical properties of the deposit and the plating characteristics of the solution, Part 2 to the corrosion-resistance of the deposits. It was found that, as the length of service of the solution increased, the ductility of the deposits tended to fall, the internal stress to increase and the bright-plating range to contract. The amount of organic impurity in the solution increased with time, and though its nature was not known, the presence of this impurity was considered the probable cause of the observed deterioration in the properties of the deposits.

At intervals during the operation of the pilot plants in which these tests were conducted, thick deposits were produced for subsequent examination with respect to composition and microstructure. The results of such examination are recorded in the present paper.

Values obtained by determination of the carbon, oxygen, hydrogen and nitrogen contents of the

deposits are plotted against the length of service of the respective solutions, and variations in microstructure (as a function of ageing of the solutions) are illustrated by photomicrographs.

The results reported confirm the previous findings with respect to the accumulation of organic impurities and their responsibility for the deterioration in the properties of the deposits. There was evidence of increasing incorporation of organic substances in the deposits as the solutions aged, and of a definite relationship between mechanical properties and the amount of organic material incorporated. In the 'Super Gleamax' solution all three addition agents contained carbon, hydrogen and oxygen; two of them contained also nitrogen and sulphur. Analysis of the deposits gave proportions of the various elements which corresponded roughly with those to be expected on the assumption that the only materials incorporated in the nickel coatings were addition agents and their deposition products.

Changes in the structure of the 'Super Gleamax' coatings as the solution aged appeared to bear some relationship to the properties of the deposit; a finer structure with prominent striations was characteristic of the brittle deposits obtained when the solution was relatively highly contaminated after long operation. The 'Efco-Udylite' coatings, on the other hand, exhibited this same structure, with no appreciable variation, throughout the whole period of operation of the solution. That no structural change occured in the latter deposits might, it is considered, be a consequence of the fact that whereas in the 'Efco-Udylite' solution it remained at a high level throughout, in the former solution the concentration of anti-stress agent increased during the period of operation.

Addition of 'M730' (which consisted principally of anti-stress agent) lowered the total amount of material incorporated in the 'Super Gleamax' deposits, with consequent rise in ductility. Whether the anti-stress agent replaces a much larger amount of other organic substances in the deposit or simply reduces the amount of material adsorbed and incorporated, without itself being included in the deposit, is discussed by the authors. The evidence available is not sufficient to warrant definite conclusions, and speculation as to the causes of the phenomenon (which could have important practical and theoretical implications) cannot be confirmed without further investigation.

---

D. A. FANNER and R. A. F. HAMMOND: 'Properties of Nickel Electrodeposited from a Sulphamate Bath', *Paper No.* 12.

See *Trans. Inst. Metal Finishing*, 1958/59, vol. 36, Pt. II, pp. 32–42.

An abstract of this paper was published in *Nickel Bulletin*, 1959, vol. 32, No. 4, pp. 107–8.

---

L. W. OWEN: 'The Deposition of Nickel from Nickel Carbonyl', *Paper No.* 8.

While, in general, 'dry' methods of depositing metals (e.g., by spraying, vacuum-metallizing, chromizing) cannot compete commercially with 'wet' electrolytic methods, in certain applications their use is amply justified by the results. Many metals of direct interest to the atomic energy industry (such as molybdenum, tungsten, tantalum, niobium) are, for example, difficult to deposit electrolytically. On metals (magnesium, uranium, etc.) which tend to react deleteriously with the electrolyte during electroplating, deposition of nickel by thermal decomposition of a gaseous nickel compound offers a method of producing coatings of considerable thickness, comparable in properties to those of nickel electrodeposits. The advantages of, and techniques used in, nickel plating viâ nickel carbonyl are reviewed by the author in the present paper.

By way of introduction, the characteristics of the nickel-carbonyl process are discussed in relation to those of other vapour-deposition techniques. Nickel carbonyl has the advantage of being highly volatile; it involves no problems of condensation, the nickel deposit is not embrittled by the co-deposited carbon, and, in addition, rates of deposition are extremely high ($30 \times 10^{-3}$ in./hr.).

Deposition of nickel from the carbonyl may be effected by two techniques: the low-pressure and the atmospheric-pressure methods. Details are given of the operation of, and the equipment needed for, both processes. Consideration is given also to the significance of each of the principal variables involved in plating (temperature, rate of flow of vapour, rate of flow of diluent gas, and total pressure), and in the final section of the paper the author discusses the properties obtainable in gas-deposited nickel coatings.

---

H. SZMIDT, T. ZAK and Z. KWIATOWSKI: 'Rapid Quantitative Methods for Determination of Brighteners, Levellers and Anti-Pitting Agents in Nickel Electroplating Baths', *Paper No.* 9.

See *Trans. Inst. Metal Finishing*, 1958, vol. 36, Pt. I, pp. 17–21.

An abstract of this paper was published in *Nickel Bulletin*, 1959, vol. 32, No. 3, p. 75.

---

**Alloy Plating**

B. H. PRISCOTT: 'Electrodeposition of Copper-Nickel Alloys', *Paper No.* 10.

See *Trans. Inst. Metal Finishing*, 1959, vol. 36, Pt. III, pp. 93–6.

Despite the extensive use of copper-nickel alloys for applications involving high electrical resistance, corrosion-resistance or particular thermo-electric characteristics, little work has been carried out to investigate the feasibility of producing such alloys by electrodeposition on a commercial scale.

Preliminary experiments revealed that, of the solutions suggested in the literature as suitable for deposition of copper-nickel alloys, citrate electrolytes gave the most satisfactory coatings. On the basis of this finding, the author concentrated his efforts

on determining optimum conditions for deposition of the alloys from solutions of the following basis composition (designed to give a total metal concentration of 0·19 *M*), to which 10, 20, 40, 75 or 160 g./L. of trisodium citrate were added.

| Nickel Sulphate aq. g./L. | Copper Sulphate aq. g./L. | Sodium Chloride g./L. |
|---|---|---|
| 54 | — | 2 |
| 42 | 10·3 | 2 |
| — | 48 | 2 |

Depending on the composition desired in the deposit, the anodes were selected from nickel, 'Monel' (67 per cent. nickel), and 50–50 or 75–25 cupro-nickel.

Using small volumes (500 ml.) of solution, the influence of the following variables was studied: (1) presence of chloride ion, (2) citrate concentration, (3) solution concentration, (4) pH, (5) copper-nickel content of the solution, (6) temperature, (7) agitation, (8) current density. The results obtained for each variant are presented and discussed.

It was found that sound adherent copper-nickel deposits, covering a wide range of composition, could be obtained from citrate solutions, for which the conditions below were established as optimum.

| | |
|---|---|
| Citrate concentration | 75 g./L. |
| Total metal concentration (as sulphates) | 0·19 *M* |
| pH | about 5 |
| Temperature | 55°C. |
| Current density | 20 amp./sq. ft. (2·16 amp./dm.$^2$) |

The composition of the deposit varies with variation in the composition of the solution and in the cathode current density, but is not markedly affected by temperature of operation or by agitation of the solution. It is controlled by modification of the ratio of the metal content of the solution (and, in this connexion, the paper includes a graph which indicates the concentration required for deposition of alloys of a given composition). Anode efficiency is increased by addition of sodium chloride in amounts of about 2 g./L. In the solutions containing a small proportion of chloride, anode efficiency is substantially 100 per cent.; cathode efficiency varies, however, from 50 to 80 per cent., depending on temperature, current density and composition of the electrolyte. Hardness and contractile stress exhibited by a 55–45 copper-nickel coating were somewhat greater than that of nickel deposited from a Watts solution. Exploratory measurements of throwing power indicate that the solution is capable of very uniform distribution of metal. It is anticipated that further study, covering prolonged operation of the solutions, should yield the information necessary for control and maintenance on a commercial scale.

---

W. T. LEE: 'Bronze Plating from Modified Stannate Cyanide Baths', *Paper No.* 11.

See *Trans. Inst. Metal Finishing*, 1958/59, vol. 36, Pt. II, pp. 51–7.

An account is given of the variation in composition of bronze deposits as a function of solution composition and plating conditions. The factors necessary for correct balance of anode and cathode efficiencies are discussed, and the advantages of bronze plating, compared with nickel and copper plating, are reviewed. The use of potassium-base bronze-plating solutions results in improved electrode efficiencies, and satisfactory results have been obtained from pilot-plant operation of a lithium-base electrolyte.

---

V. R. RAMANATHAN: 'Hardness of Electrodeposited Speculum Metal and Other Tin-Copper Alloys', *Paper No.* 15.

See *Trans. Inst. Metal Finishing*, 1958/59, vol. 36, Pt. II, pp. 48–50.

The paper presents the results of an examination of the hardness of deposits having tin contents of 10–86 per cent.

---

**Embrittlement, Fatigue and Hardness**

R. L. SAMUEL and N. A. LOCKINGTON: 'Brittle Fracture of Ultra-High-Tensile Steels in Relation to Surface Coatings', *Paper No.* 13.

When heat-treated to near their maximum strength level, the ultra-high-tensile steels are known to be unusually sensitive to hydrogen embrittlement, which might be induced as a result of treatment before or during electrodeposition of the corrosion-resisting coatings sometimes required in the applications for which such steels are used. The work described was carried out to determine the influence of various types of corrosion-resisting coatings on brittle fracture of a steel of the following nominal composition: carbon 0·4, silicon 1·5, manganese 1·5, chromium low, nickel 1·75, molybdenum 0·4, vanadium 0·2, per cent.

The test programme was designed (1) to assess the conditions of fracture of the heat-treated material coated, by conventional electroplating methods, with zinc, cadmium, nickel, chromium, etc., and (2) to develop other types of coating, application of which, using non-electrolytic methods (e.g., vapour deposition), would involve little or no generation of nascent hydrogen. Protective coatings selected for investigation were deposited by the following methods:

Electrodeposition of zinc
" " " cadmium
Deposition of zinc from the gas phase
" " aluminium under high vacuum
Application of hard silicone stoving lacquer
Electrodeposition of nickel
" " " " + chromium

Fracture characteristics of coated and uncoated notched specimens were determined by means of sustained-load tests, at loads, in the absence of

corrosive media of the order of 80 per cent. or during corrosion testing, of 65–75 per cent. of the nominal fracture strength of the steel. Conditions of corrosion testing under load were designed to simulate storage conditions and atmospheric, salt-water or sulphur attack. (The tests reported, however, relate mainly to those involving intermittent exposure to 3 per cent. sodium-chloride solution.) The effect, on unprotected specimens, of deliberately induced hydrogen embrittlement was also studied. Test pieces and test apparatus are described in detail.

The results are recorded in tabular form. The conclusions to which they give rise are summarized by the authors as follows:

'(1) The use of test-pieces of small cross-section demonstrated the need for very accurate control during heat-treatment of the steel. There is also evidence to show that after the normal tempering at 400°C. for 1 hour the material is sensitive to further periods of tempering even at temperatures well below the initial 400°C. soaking. Use of the lowest practical temperature is therefore important during any subsequent treatment involving re-heating.

'(2) No immediate embrittlement of the notched specimens has been found as a result of cadmium plating, but such specimens loaded at a stress of 80 per cent. of the fracture strength have failed within 10–100 hours of the application of the stress. This remark applies to specimens heat-treated to a notch-fracture strength of 160–170 t.s.i. (252–268 kg./mm.$^2$). Zinc-vapour-coated specimens do not appear to show delayed fracture.

'(3) At a strength level of 180–190 t.s.i. (284–300 kg./mm.$^2$) and a percentage load of 70–80, nickel/chromium-plated specimens give generally inconsistent results, failure occurring within periods varying from a few minutes to 60 days or more. Nickel-plated specimens are more consistent and, in the absence of a corrosive agent, do not generally fail under these conditions. Zinc-vapour-coated specimens behave much as the nickel-plated samples.

'(4) The corrosive action due to intermittent spray with 3 per cent. sodium-chloride solution invariably resulted in the rapid failure of both coated and uncoated specimens at stresses of the order of 70 per cent. of the notch-fracture strength. Whilst it is not possible to give a quantitative measure of the sensitivity to sodium-chloride corrosion, the approximate resistance to this type of corrosion, in descending order of sensitivity, is: cadmium electrodeposits, nickel/chromium electrodeposits, zinc-vapour deposits, aluminium vacuum deposits, nickel electrodeposits, hard silicone lacquer.

'In the main, silicone-lacquered specimens showed little or no sensitivity to sodium-chloride corrosion.

'There can be little doubt with respect to the detrimental effect of this type of corrosion; not only did the specimens subjected to spray fail within a short time, whilst the uncorroded controls were unaffected, but it is significant that if, after some 14–21 days' sustained load, the controls are sprayed in their turn, fracture rapidly takes place.

'There is evidence that the failure is related to the mechanism of the corrosion reaction rather than to the degree of corrosion.

'(5) Fracture at a stress of some 70 per cent. of notch strength can be obtained on uncoated specimens within a few minutes to a few hours of deliberately charging the specimen with nascent hydrogen. This provides additional confirmation that nascent hydrogen generated at or near the surface of such material heat-treated to a high strength level is sufficient cause for failure.

'There is not, however, enough evidence to assert that hydrogen embrittlement is a necessary factor in the failure, unless it is assumed that, whenever failure occurs during corrosion, the fracture results from the formation of nascent hydrogen at some stage of the reaction.'

---

K. SACHS and S. H. MELBOURNE: 'Hydrogen Embrittlement of Steel by Pickling and Cadmium Plating', *Paper No.* 14.

An investigation was made of the effects, on the ductility of mild-steel screw wire, of electrolytic cathode charging and subsequent ageing at various temperatures. Embrittlement resulting from hydrogen absorption during routine plating operations was studied, using carbon-steel coil springs and slugs cut from the screw wire.

---

**Fundamental Studies and Techniques**

A. K. N. REDDY and H. WILMAN: 'Structure and Growth of Iron and Chromium Electrodeposits on Copper Single Crystals', *Paper No.* 16.

See *Trans. Inst. Metal Finishing*, 1959, vol. 36, Pt. III, pp. 97–106.

---

M. CLARKE and S. C. BRITTON: 'An Electrochemical Method of Obtaining an Index of Porosity of Metal Coatings', *Paper No.* 17.

See *Trans. Inst. Metal Finishing*, 1958–59, vol. 36, Pt. II, pp. 58–66.

An abstract of this paper was published in *Nickel Bulletin*, 1959, vol. 32, No. 4, pp. 108–9.

---

O. S. HEAVENS: 'Optical Techniques for Studying Metal Surfaces', *Paper No.* 18.

The author discusses five optical methods of studying the surface finish of polished or electrodeposited surfaces: straight microscopy, interference microscopy, light-profile microscopy, multiple-beam interferometry and measurement of surface reflectivity.

The first four are dealt with briefly, since they have been adequately described elsewhere; the fifth, the application of which to metal finishing is believed to be new, is discussed in more detail. Results obtained from examination of polished brass and electrodeposited coatings (cadmium, nickel, zinc, silver and copper) are presented and discussed. Application of the techniques to study of oxidized metal surfaces is described.

---

H. R. THIRSK and W. K. F. WYNNE-JONES: 'Some Techniques in Studying the Rates of Deposition and Formation of Inorganic Films on Metal Surfaces', *Paper No.* 19.

The authors review relevant experimental and theoretical methods, and suggest alternative techniques which their own experience of fast anodic reactions has shown to be of value in the study of metal deposition.

---

T. DE GROMOBOY and L. L. SHREIR: 'A Resistance Method for Studying Rates of Reaction during Chemical Polishing', *Paper No.* 20.

The apparatus described permits the rate of dissolution of a metal to be determined continuously and without interference with the course of the process. The metal, in the form of a thin wire, is wound non-inductively round a glass rod which can be rotated at constant and reproducible speeds. An alternating current is passed through the wire and the potential is measured, thus enabling the electrical resistance, and hence the radius of the wire, to be calculated. Results obtained for the dissolution of aluminium in a phosphoric/nitric-acid chemical-polishing solution are given.

---

**Organic Finishing**

R. E. SHAW: 'Developments in Metal Pre-Treatment', *Paper No.* 21.

See *Trans. Inst. Metal Finishing*, 1959, vol. 36, Pt. III, pp. 107–12.

The emphasis of the paper is on preparation of metals for painting.

---

H. H. NORCROSS: 'Measurement of Paint Finishing Costs', *Paper No.* 22.

---

D. E. J. CUNNINGHAM: 'Recent Advances in Plastic Coatings for Metals', *Paper No.* 23.

An outline is given of current commercial practice in applying homogeneous plastic coatings to metals for decoration or protection.

---

R. L. YEATES: 'The Impact of Organic Chemistry on Metal Finishing', *Paper No.* 24.

The author discusses the significance of various synthetic organic chemicals in relation to metal finishing.

**Blackening of Nickel Anodes During Electrodeposition of Black Nickel**

T. C. FRANKLIN and J. GOODWYN: 'The Mechanism of Blackening of Nickel Anodes.'

*Jnl. Electrochemical Soc.*, 1959, vol. 106, Mar., pp. 269–71.

It has been observed by earlier investigators that when black-nickel coatings were being deposited from a solution of the type shown below, the nickel anode, as well as the cathode, became blackened. This paper reports a study of the composition of the black deposit formed on the anode and of the mechanism by which it is formed.

The solution used was of the following composition:

| | *g./L.* |
|---|---|
| $NiSO_4.6H_2O$ | 70 |
| $(NH_4)_2SO_4$ | 37 |
| $ZnSO_4.7H_2O$ | 34·3 |
| KSCN | 17·9 |

The solution was operated at a pH of 5·0, at 30°C., with a current density of 11 amp./dm.$^2$.

Experiments made to determine the influence of the individual constituents of the bath leads to the conclusion that the black coating formed on the nickel anodes is due to reactions arising from the presence of potassium thiocyanate. The coating consists of nickel sulphide, and it is indicated that formation takes place according to the following series of reactions:

$$Ni \rightarrow Ni^+ + e$$
$$2Ni^+ + CNS \rightarrow NiS + CN^- + Ni^{++}$$

**Effect of Purity of Water in Electroplating Solutions**

K. SOMMER: 'Effect of Biologically Polluted Waters in Electrodeposition.'

*Electroplating*, 1959, vol. 12, Mar., p. 105.
From *Metallwaren-Industrie und Galvanotechnik*, 1958, vol. 49, p. 351.

The author emphasizes the danger of discontinuities occurring in electrodeposited nickel coatings as a result of using, for the electrolytes, water contaminated by fungoid or other growths which may occur in water from lakes or other inadequately purified sources. Typical examples are quoted from the author's experience, and an illustration shows a filiform defect in a polished nickel deposit on a mirror, indicating interrupted deposition of metal resulting from non-metallic inclusions.

**Electroless Nickel Plating of Carbon**

H. J. WEST: 'Electroless Nickel Plating of Carbon.'

*Metal Finishing*, 1959, vol. 57, Feb., p. 64.

Certain components of missiles are made from carbon, and in some cases it has been found necessary to produce, on these parts, an adherent and sound metal coating, e.g., prior to flame-plating with tungsten. Electroless nickel deposits have been found to satisfy requirements, and this article gives

details of procedure for preparation of the carbon surface and deposition of the coating.

The part is cleaned by immersion for a few minutes in trichlorethylene, or rubbing the surface of the carbon with a clean cloth, avoiding contact with the hands.

After cleaning, the surface is activated by wrapping iron wire round the work or placing it on an iron-wire screen in the electroless-plating solution. Coverage proceeds at a slow rate until the carbon surface is completely covered with nickel, after which the rate increases rapidly. Approximately four hours' plating is required to secure the minimum thickness of about 0·001 in. (0·025 mm.) required as a basis for tungsten flame plating.

The solution recommended is:

| | | |
|---|---|---|
| Water | 10 gal. | 45·45 L. |
| Nickel chloride | 5 lb. | 2·2 kg. |
| Sodium citrate | 8 „ | 3·6 „ |
| Sodium hypophosphite | 1 „ | 0·45 „ |

After complete dissolution of the salts (in water at about 150°F.; 65°C.) the solution is raised to a slow boil and maintained in that condition during plating. As the reaction slows down sodium hypophosphite is added in one-ounce (28-g.) portions until the required rate of plating is again established.

### Co-Deposition of Tungsten and of Molybdenum with Nickel and Other Metals

W. H. SAFRANEK and L. E. VAALER: 'Progress in Alloy Plating: 1. Tungsten and Molybdenum Alloys.'
*Plating*, 1959, vol. 46, Feb., pp. 133–43.

In 1940 Faust published a comprehensive review of information on electrodeposition of alloys, which included discussion of the literature relating to deposition of tungsten and of molybdenum alloys (see *Trans. Electrochemical. Soc.*, 1940, vol. 78, pp. 383–417). Since 1940 more than 50 items of literature on this subject have been published, but although these alloy systems have unusual electrochemical and metallurgical interest, few practical applications have developed, due to lack of ductility in the alloy deposits and the difficulty of controlling the plating solutions.

This paper comprises a commentary on the literature from 1940 onwards. The information available from the various sources indicates that iron, cobalt and nickel are the only alloying elements which make possible co-deposition of substantial amounts of tungsten or molybdenum. Alloys of these metals with other elements can be produced, but very high current densities are required and current efficiency is very low; also, the amount of tungsten or molybdenum is in many cases so small as to leave doubt as to whether the deposit is really in alloy form or whether the tungsten or molybdenum is merely adsorbed on the surface or occluded as a salt.

The authors of this review summarize the compositions of solutions which have been proposed for deposition of binary and complex alloys of tungsten and of molybdenum, giving details of operating conditions and of the nature and properties of the deposits obtained. The final section of the review is concerned with the mechanism of co-deposition of tungsten and of molybdenum with other metals, and some suggestions are made for lines of future research which might lead to solution of some of the problems which have been encountered. The review is based on literature referred to in a *bibliography* of 60 items.

---

Reference is given below to a paper of related interest:

T. T. CAMPBELL: 'Electrodeposition of Molybdenum.'
*Jnl. Electrochemical Soc.*, 1959, vol. 106, Feb., pp. 119–23.

Report of work in which attention was directed to the electrodeposition of molybdenum from non-aqueous media such as liquid ammonia, formamide, acetamide, hydrazine and other organic solvents, and to the preparation of pure anhydrous molybdenum halides.

### Electrodeposited Nickel/Chromium Coatings: Influence of Thickness and Quality of Chromium

E. J. SEYB and W. H. ROWAN: 'Thicker Decorative Chromium for Better Corrosion-Resistance.'
*Plating*, 1959, vol. 46, Feb., pp. 144–9.

The authors point out that there is a growing recognition of the significance of the quality of the surface layer of chromium, as affecting the corrosion-resistance of (copper)/nickel/chromium coatings. There has, however, been some divergence of opinion with regard to optimum thickness: 0·02 mil has been advocated by some investigators, whereas others claim to have found added protection from a thickness of as much as 0·1 mil.

This paper reports tests in which panels carrying various thicknesses of chromium (normal or crack-free), over various thicknesses of copper+nickel, were evaluated by the copper-accelerated acetic-acid spray test, by the 'Corrodkote' test, and by atmospheric exposure. The results reported (which are illustrated by photographs demonstrating the condition of the panels after test) lead the authors to the following conclusions:

On thin undercoatings protection afforded by conventional, cracked chromium increases with thickness up to about 0·02 mil, and then falls off again, presumably because the development of the cracks exposes the undercoat, or the stresses caused by the cracking cause similar cracks in the nickel. With similar thickness of undercoat, increasing thickness of crack-free chromium has a progressively beneficial effect, and no change is found at the 0·02 mil thickness.

On heavy undercoatings (about 1·5 mil or more of *ductile* nickel) protection provided by the chromium increases with increased thickness, regardless of whether the chromium is cracked or not. This conclusion is subject to the limitation that the nickel undercoating must be sufficiently ductile to prevent its

being penetrated as a result of cracking in the chromium, and in this connexion it is suggested that greater attention should be paid to ductility as a desirable feature in bright-nickel deposits. It is strongly recommended that the plating industry should gradually introduce greater thicknesses of chromium, until the goal of 0·1 mil or more on significant surfaces can be regularly specified, and that, wherever possible, plating conditions should be such as to produce crack-free chromium.

**Corrosion-Resistance of Copper/Nickel/Chromium Electrodeposited Coatings**

A. H. DU ROSE and W. J. PIERCE: 'Copper/Nickel/Chromium and Corrosion Protection.'

*Metal Finishing*, 1959, vol. 57, Mar., pp. 44–50, 54.

In 1956 the authors published a paper in which they drew attention to the inconsistent quality of electrodeposited coatings, and urged that, due to generally poor reproducibility, it was impossible, from the standpoint of protection against corrosion, to draw generalized conclusions from the results of any one test, even though the method of test might be reasonably discriminating. (*Plating*, 1956, vol. 43, p. 239; see abstract in *Nickel Bulletin*, 1957, vol. 30, No. 6, p. 88.)

In the interim their argument has received much support from conflicting results of corrosion tests reported in the literature, and they therefore consider it advisable to review the present position and to publish some relevant experimental data.

As an introduction to the paper, a summary is made of the main questions which are now receiving attention by producers and users of plated parts. These questions are quoted below, together with conclusions and comments which the authors consider to be justified by the results of their own experimental investigations, correlated with published data and practical experience.

'*Question* 1. Are plated parts, especially on cars, giving as good corrosion-resistance as was obtained in the past ?

'*Answer*. Discounting extreme recesses, and taking into consideration a supposedly more corrosive atmosphere, plated parts are as good now as they were in 1938. It is probably questionable whether any factual proof is available to show that nickel plating is not as good to-day as it was 20 years ago. However, the recollection of most people is that this is the case and, while the use of the organic-type bright nickel might be some small factor, the authors believe that two other often overlooked factors are of much more importance. One of these is the more corrosive atmosphere in most urban areas, and the other is the more complicated parts which are plated to-day. With regard to the atmospheric cause of deterioration, it will be found that most air-pollution data show an increase in constituents which are corrosive to nickel and chromium, and even without analytical data the increase in vehicle registration would point to the same conclusion. With regard to the increase in complexity of the parts plated, this has forced the advance of the art and science of plating, but there is a point beyond which the cost is substantially increased.

'*Question* 2. Are results obtained at one outdoor exposure site representative of those obtained at other sites ?

'*Answer*. Between two different types of outdoor exposure sites the order of merit of different copper/nickel/chromium coatings is usually the same, with some unexplainable reversals. It is not unusual, however, for two coatings to be different at one site and practically the same at another site. (See below for the authors' comments on methods of evaluating and rating corrosion.)

'*Question* 3. Do accelerated test results predict serviceability ?

'*Answer*. Similar differences in order of merit are obtained between outdoor exposure sites and accelerated corrosion tests as are obtained between different outdoor exposure tests.

'*Question* 4. Is a copper undercoat prior to nickel of any value ?

'*Answer*. A copper undercoat prior to grey nickel or a sulphur-free nickel deposit is of practically no benefit. A copper undercoat prior to a sulphur-containing nickel is frequently beneficial. The improvement may be equal to that of an equal additional thickness of sulphur-containing nickel. When corrosion does occur, the copper/nickel/chromium-plated article will be more unsightly, due to crater-rusting, than would be the case for nickel/chromium.

'*Question* 5. Does bright nickel have as good corrosion-protective value as grey nickel ?

'*Answer*. Sulphur-containing semi-bright or bright nickel deposits do not exhibit as good corrosion protection as do sulphur-free deposits.'

With regard to evaluation and rating of corrosion the authors emphasize the generally recognized difficulty imposed by the variations in the conditions of test used by various investigators, the factors which may influence corrosion attack within any given period (e.g., differences in behaviour under atmospheric exposure according to the season at which the exposure is made), and the criteria adopted for assessment of attack and rating of protective value. For these reasons, absolute correlation among available test data cannot be expected, but useful information can be obtained by the method which the present writers have adopted, that of examining the behaviour of panels or parts plated with various types and thicknesses of composite copper/nickel/chromium coating under a given test and of checking such results in the light of the behaviour of identical coatings under other standard exposure or accelerated tests.

The test specimens compared were representative of (copper)/nickel/chromium coatings of varying thickness, the variables in the case of nickel including

also the use of sulphur-containing and/or sulphur-free coatings. Comparisons are made under the following conditions:

One year's exposure at sites of varying atmosphere, correlated with behaviour under the 'Corrodkote' test.

Atmospheric and 'Corrodkote' ratings as a function of thickness of bright nickel and of chromium.

Influence of sulphur-free and sulphur-containing nickel underlays, on behaviour in atmospheric and 'Corrodkote' tests.

Behaviour under 'Corrodkote' test in comparison with resistance to attack in (1) acetic-acid/salt-spray, and (2) accelerated acetic-acid/salt-spray tests.

These data, which form the main basis of the answers given to the questions listed on p. 146, show fair all-over correlation of behaviour under the respective types of exposure, but it is emphasized that some variations will be found, and that closely parallel results under the various tests are not to be anticipated. It can, however, be concluded that if in atmospheric tests, there are large differences between two types of coating at one site, the differences will generally be in the same direction at another site. The 'Corrodkote' test shows, in most cases, a useful indication of behaviour under atmospheric exposure, and the data presented show 'reasonable correlation' between the two acetic-acid/salt-spray tests and the 'Corrodkote' test.

The authors make some comments also on the nature of the pinhole corrosion observed in a deposit comprising sulphur-containing semi-bright nickel + organic bright nickel, and on surface pitting of a sulphur-free-nickel/bright-nickel duplex deposit.

Attention is called in this paper, as in several others recently published, to the influence, on protective value, of the nature and thickness of the final chromium coating. Most of the specimens prepared by the authors were plated with a higher-than-normal thickness of 'high-temperature chromium' and tabular data indicate the better protective value of such coatings. It is noted also that some additional protection can be obtained by using a double layer of chromium: this effect can be produced by interrupting the current during plating or by using a chromium-plate/rinse/chromium-plate cycle. A warning is given that colour-wiping the chromium coating lessens its protective value, but this effect can be substantially offset by re-immersion of the work in the chromium-plating solution, and rinsing. Lightly wiping with magnesia does not have any harmful effect on protective value.

The paper closes with a note on conditions which must be observed in order to obtain accurate results when determining the thickness of chromium by the hydrochloric-acid spot-test method. Factors involved are (1) the grade of acid used, (2) the interpretation of the end-point of the reaction, and (3) the effect of the temperature at which the coating has been deposited, on the rate at which the chromium dissolves in the test acid.

**Influence of Nickel and Nickel-Chromium Underlayers on Adhesion of Evaporated Aluminium Films**

C. WEAVER and R. M. HILL: 'Adhesion of Evaporated Aluminium Films with Underlayers of Nickel, Cobalt and 'Chromel'.'

*Philosophical Magazine*, 1959, vol. 4, Feb., pp. 253–66.

Vacuum-evaporated aluminium films have been extensively used for the production of reflecting surfaces, but advantages of aluminium as an optical reflector are diminished to a certain extent by its poor adhesion when deposited directly onto glass, and, as a means of increasing durability and adhesion, it has been common practice to interpose a thin layer of chromium between the glass and the aluminium. The influence of chromium in this respect was investigated by WEAVER and HILL (*ibid.*, 1958, vol. 3, p. 1402). Experiments to study the effects of nickel, cobalt, and nickel-chromium underlays are described in the present paper.

Nickel, cobalt and aluminium films were deposited on glass slides, and composite layers of nickel/aluminium and cobalt/aluminium were also prepared. In some of the experiments the 80–20 nickel-chromium alloy 'Chromel' was also used as undercoating. Measurements of adhesion were made on the films in the as-deposited condition and at suitable time intervals after ageing at room temperature or at 120°C. The results are presented in curves showing variation of adhesion as a function of the nature and thickness of the underlayer and of the time of ageing.

It was found that in the as-deposited condition the adhesion of composite nickel/aluminium films was fairly high, except where the nickel undercoating was less than 30Å. Ageing at room temperature for two weeks gave a similar curve with respect to thickness of undercoat, though considerably higher values were obtained; ageing at 120°C. for three days lessened adhesion and highest values were obtained with the thinnest films. Aluminium films with cobalt underlay showed poor adhesion.

The results for 'Chromel' are considered particularly promising. Increase in adhesion of the aluminium due to interpolation of this alloy between the glass base and the aluminium coating was comparable with the best results obtained with nickel, and noticeably better than those obtainable with an underlayer of chromium. Varying the ageing temperature had little influence on the results: no pronounced difference in effect was found between thick and thin films of the alloy, and 'Chromel' has the further advantage, over nickel and chromium, of being relatively easy to evaporate.

The difference in behaviour of the respective films is shown to be due to formation of intermetallic compounds at the interface, causing a type of age-hardening which may result in either decrease or increase in adhesion, according to the compound formed and the condition of ageing.

**Oxidation-Resistant Coatings for Molybdenum**

See abstract on p. 158.

## NON-FERROUS ALLOYS

### Nickel-Aluminium-Bronze Propellers: Production and Properties

A. J. SMITH: 'Some Foundry Problems in the Development of a New Marine Propeller Alloy.'
*Modern Castings*, 1959, vol. 34, Jan., pp. 55–70.

Manganese-bronze propellers have for many years given satisfactory service, but advances in marine propulsion have necessitated development of a material giving improved wear-resistance and better capable of giving long life under increasingly severe service conditions. Although the superior properties of nickel-aluminium bronzes have for some time been firmly established, the cost of changed production technique and other factors precluded any premature changeover. The matter has, however, been studied in various foundries, and this paper describes experience by a company which produces castings of this type ranging from 6,000 to 120,000 lb. (3 to 60 tons) rough weight.

In the first stage of investigation efforts had been made to modify the composition of the standard manganese-bronze propeller alloy, but although, by additions of nickel or tin, some improvements were obtained in wear-resistance and mechanical properties, the conclusion was reached that a fundamentally different type of alloy was needed for full realization of the properties required. Extensive studies within the nickel-aluminium-bronze range of composition, including laboratory and simulated service tests, and foundry tests to determine melting and casting characteristics, led to the selection of an alloy of the following composition as giving the optimum combination of properties: copper 78–81, nickel 4·5–5·5, iron 3·5–5·5, manganese 0·5–1·0, aluminium 9·0–10·3, lead 0·01 max., other elements (including zinc and tin) 0·5 max., per cent. The properties of such alloys are compared, in this paper, with those of standard manganese bronze.

The author's chief concern is with foundry experience in establishing the technique most suitable for production of propeller castings in the new alloy. A detailed account is given of experimental work on melting conditions (including particular reference to the position of the burner and to use of fluxes); gas absorption is discussed at length, various types of moulding material are compared, and recommendations are made on selection of raw materials and on feeding of production castings. The information given is essentially practical and informative.

In the second section of the paper comparison is made of manganese-bronze and nickel-aluminium-bronze propellers, on the basis of engineering properties, and from the standpoint of service experience. Curves illustrating erosion-corrosion resistance of the two materials demonstrate clearly the superiority of the new alloy, and the following further advantages are also noted:

Only minor variations in properties are found between heavy and light sections.

It has greater resistance to fouling by marine organisms.

Nickel-aluminium bronze retains its original smooth machined surface over a long period, thereby maintaining a high propeller-efficiency factor.

Nickel-aluminium-bronze is some 10 per cent. lighter than manganese bronze, and because of its higher strength, can be designed to thinner sections; e.g., loading stresses on the tailshaft and bearings are reduced, thus permitting use of lighter shafts. Costs are appreciably reduced.

The low notch-sensitivity of nickel-aluminium bronze contributes significantly to its value as a propeller material.

Nickel-aluminium bronze propellers can be easily repaired by the inert-gas welding process.

The superiority of nickel-aluminium-bronze propellers is being convincingly proved by the reports which are gradually accumulating with regard to service in ocean-going liners, in craft operating in sandy waters, and in icebreakers.

The properties characteristic of the material are leading also to its employment in various other applications in which strength, wear-resistance, and relatively low density are advantageous.

### B.S. Specifications for Nickel Alloys

See abstract on p. 139.

### Diffusion and Oxidation of Metals: Literature Reviews

See abstract on p. 138.

### Electrical and Thermal Resistivity of Alloys at Low Temperatures

See abstract on p. 138.

### Anisotropy and Magnetostriction Constants of Single Crystals of Nickel-containing Alloys

See abstract on p. 149.

### Analytical Chemistry in the Atomic Energy Field

See abstract on p. 138.

### Determination of Cobalt in Nickel and Nickel-containing Steels

See abstract on p. 151.

---

## NICKEL-IRON ALLOYS

### Properties of Magnetic-Amplifier Core Materials

G. SIDERIS: 'Soft Magnets for Amplifiers.'
*Electronics*, 1959, vol. 32, Feb. 6, p. 55.

Typical magnetic properties are tabulated for new and standard magnetic-amplifier core materials.

The alloys for which information is given are grouped according to composition:

(1) Grain-oriented nickel-iron alloys containing 45–50 per cent. nickel (e.g., 'Deltamax', 'Hipernik V', 'Orthonol', 'Orthonik', 'Permeron').

(2) Nickel-iron alloys ('High Perm 49', 'Hipernik', '45 Permalloy', '65 Permalloy', '4750 Allegheny').

(3) Complex nickel-base alloys ('4-79 Permalloy', 'Supermalloy', 'Hy Mu 80', 'Dynamax', 'Mu-metal', '1040 Alloy', 'Supermendur').

(4) Grain-oriented 3-3·5 per cent. silicon-iron alloys ('Hipersil', 'Silectron', 'Magnesil', 'Alphasil', 'Tran-Cor 3X').

(5) Nickel-zinc + copper ferrites ('Ferramic H', 'Ferramic H-1').

The D.C. magnetic properties of cube-oriented and grain-oriented 3 per cent. silicon steels are also listed.

**Anisotropy and Magnetostriction Constants of Single Crystals of Nickel and Nickel-containing Alloys**

R. C. HALL: 'Single-Crystal Anisotropy and Magnetostriction Constants of Several Ferromagnetic Alloys.' *Wright Air Development Center, Tech. Note* 58-127, Apr. 1958; 41 pp. *P.B.* 151036.

The report records the results of the first part of research planned to determine the effects of nuclear irradiation on the magnetic properties of ferromagnetic materials, in particular, its influence on the anisotropy and magnetostriction of single crystals of a wide range of 'soft' ferromagnetic metals and alloys. The experiments were expected to indicate not only the types of material least susceptible to damage but also methods which could be used to minimize or prevent deterioration.

The thirty-one single crystals selected for study comprised nickel, iron, magnetite, and nickel-iron, nickel-cobalt, silicon-iron, aluminium-iron, cobalt-iron, nickel-cobalt-iron, nickel-iron-molybdenum and aluminium-iron-molybdenum alloys of various compositions. This first report is concerned with the testing of the crystals before irradiation; the effects of irradiation on the properties of the crystals will form the subject of later reports. Full details are given of the methods employed to prepare the crystals, heat-treatments to which they were subjected, and the techniques used to measure magnetostriction and anisotropy. The values obtained are compared with those reported in the literature, and, where possible, the data are related to the properties of polycrystalline materials. The effect of order/disorder reactions was also determined.

In general, data determined for the nickel-iron and silicon-iron systems agree very well with recently reported values. New data are, however, presented for cobalt-nickel and cobalt-iron alloys.

**Influence of High Temperature on Performance of 'Alnico V' and 'Alnico VI' Permanent Magnets**

W. H. ROBERTS and D. L. MITCHELL: 'Effects of High Temperature on Performance of 'Alnico V' and 'Alnico VI' Permanent Magnets.'

*U.S. Atomic Energy Commission, Report APEX*-384, Feb. 1957; 90 pp. Published July, 1958.

The extremes of temperature and the vibration to which future military aircraft will be subjected are relatively unknown factors in relation to the performance of the permanent magnets used in the instruments of such aircraft, but knowledge of the influence of these conditions on the properties of the magnets is essential for effective design. The investigation referred to in this report was planned to obtain the required information.

The magnets were to be studied over a temperature range of −70° to +600°C. (the emphasis being placed on long-time operation at 500°C.), and at vibration frequencies ranging from 5 to 2000 cycles/sec. combined with an amplitude sufficiently great to produce an acceleration of at least 20G. A search of literature relevant to behaviour at a test temperature of 500°C. eliminated, as unsuitable, all the available permanent-magnet materials except the nickel-aluminium-cobalt-iron-(titanium) alloys 'Alnico V', 'Alnico VI' and 'Alnico VII'. (Because of their higher magnetic energy, the subsequent tests were carried out mainly on the first two alloys.)

Analysis of the possible mechanisms by which exposure to high or low temperatures, with or without simultaneous vibration, could change the useful flux of a magnet during operation indicated the following five as being the most significant in this respect:

(1) a permanent change in the magnetization of the magnet due to cycling through two extremes of temperature;

(2) a temporary change in the magnetization of the magnet due to changes in temperature;

(3) a permanent change in the magnetic properties of the material due to changes in the structure of the material caused by holding at high temperature for a long period of time;

(4) a combination of changes in magnetization and magnetic properties due to continuous exposure to high temperature;

(5) changes in magnetization caused by exposure to a combination of either high or low temperature and vibration.

Based on these considerations, five experiments were carried out to determine (within upper and lower limits of 600° and −70°C.) the effect of each of the following variables on the useful flux of the magnets: (1) temperature cycling, (2) determination of temperature-coefficient curves, (3) ageing at 500° and 600°C. for times up to 1000 hours, (4) heat-exposure tests for 1000 hours at 500°C., (5) simultaneous exposure

to vibration and temperatures of −70°, +25° and +250°C. ('Heat exposure' is distinguished from 'heat ageing' in that in the former test the useful magnetic flux was measured during exposure of the magnet at the test temperature, whereas in the latter test measurements were made at room temperature after exposure.)

Because magnet design was known to have a pronounced effect on magnetization, three designs in each material were tested, equivalent, respectively, to a very long, a medium-length, and a very short magnet.

Test procedure and equipment are described and the data and conclusions derived from each phase of the investigation are presented *in extenso*. The general conclusions drawn are summarized below.

The results of these tests show that it is definitely practical to use 'Alnico V' and 'Alnico VI' magnets at temperatures up to 500°C. for long periods. Earlier investigations had shown that these alloys can also be used at temperatures as low as −196°C. Vibration at temperatures either above or below room temperature does not effect the useful flux of magnets made from these alloys.

Over the range up to 500°C. the behaviour of the two types ('Alnico V' and 'Alnico VI') is so similar that it is not possible to prefer one alloy over the other on that basis: selection should be made on considerations of magnet design and other operating conditions.

Use of magnets of these alloys at temperatures above 500°C. for more than a few hours does not appear practical. Deterioration of magnetic properties above about 550°C. is caused by over-ageing or excessive growth of the precipitate. It is suggested that if it is necessary to use magnets of this type between 500° and 600°C. the effective life might be lengthened to some extent by using silicon-zirconium or niobium modifications of 'Alnico V.' Such addition agents would tend to reduce the rate of precipitation or ageing.

---

## CAST IRON

### Purification of Cast Iron by Oxidation

R. H. T. DIXON: 'The Purification of Cast Iron by Oxidation.'

MOND NICKEL CO., LTD., *Publn.* 1532; 8 pp.
*Reprint* from *Brit. Foundryman*, 1958, vol. 51, Apr., pp. 197–203.

See abstract in *Nickel Bulletin*, 1958, vol. 31, No. 6, p. 165.

### Cast Irons for Die Blocks

BRIT. CAST IRON RESEARCH ASSOCN.: 'Cast Irons for Die Blocks and Similar Applications.'

*B.C.I.R.A. Broadsheet No.* 2, Jan. 1959; 4 pp.

It is pointed out that in many cases cast iron of various grades can suitably be employed for the tools required for sheet-metal forming, extruding, pressing, forging, etc. This publication gives condensed, practical information on the characteristics and uses of the following irons which can be used for applications in that field: high-phosphoric and low-phosphoric types; alloy irons (nickel-chromium and nickel-molybdenum types); grey machinable martensitic iron (alloyed with nickel and chromium); heat-treatable alloy irons; nodular- (spheroidal-) graphite irons. The broadsheet ends with reference to plain, alloy and nodular (S.G.) irons particularly suitable for use in glass-bottle moulds.

### Growth and Scaling Tests on Cast Irons

G. N. J. GILBERT: 'The Growth and Scaling Characteristics of Cast Irons in Air and Steam.'

*Brit. Cast Iron Research Assocn., Jnl. Research and Development*, 1959, vol. 7, Feb., pp. 478–566 + table.
*Research Report* 502.

Standard practice in the U.K. for steam-plant applications in which stability is important is to limit the use of cast iron to temperatures below 232°C. (450°F.). In view of advances which have been made during recent years in the metallurgy of cast iron, it has, however, been appreciated for some time that such limitation is unrealistic. In a few cases high-grade irons have been satisfactorily used for valves operating at temperatures up to 315°C. (600°F.), but general acceptance of cast iron for such applications awaits further evidence of its consistent reliability at the higher temperatures. (In America a Standard A.S.T.M. specification, prepared in collaboration with the American Society of Mechanical Engineers, covers grey-iron castings for pressure-containing parts for temperatures up to 340°C. (650°F.).)

With a view to placing at the disposal of steam engineers and others basic information which can be utilized in this connexion, the British Cast Iron Research Association is carrying out an extensive series of tests to determine the behaviour of various types of cast iron in elevated-temperature conditions. Growth data are obviously of outstanding importance, since in most cases breakdown might be expected to occur as a result of lack of dimensional stability, and information on creep-resistance will also be required. The present report covers growth and scaling tests: creep behaviour is still under examination.

Results are given of growth and of scaling in air at temperatures up to 500°C. (932°F.), after exposure for periods up to 64 weeks, and of behaviour in steam atmospheres at temperatures of 227°, 371° and 427°C. (440°, 700° and 800°F.) for periods varying between 32 and 49 weeks. Tensile and hardness tests were made on the growth specimens, before and after exposure, and the report also includes results of short-time tensile tests at temperatures up to 600°C. (1112°F.) and of impact tests on unnotched specimens of some of the irons.

The 35 materials tested were representative of plain and alloy flake-graphite, and spheroidal-graphite

irons of various types, and of blackheart malleable cast iron: the compositions were varied to permit systematic study of the effect of individual elements in the irons, and the influence of heat-treatment on high-temperature behaviour was also investigated. Full details are given of the composition of the specimens, and of the experimental test conditions, and the properties of the individual irons are reported in some 50 graphs and many tables.

These extensive results show that cast iron is structurally stable, and not subject to growth at temperatures up to 400°C. (752°F.) in air and in steam, for the periods of test used. The results confirm that the limiting temperature at present imposed in steam applications is too low: 343°C. (650°F.) appears to be a more realistic level.

## CONSTRUCTIONAL STEELS

### Vacuum-Induction Melting

See abstract on p. 138.

### Corrosion of Metals in Marine Tropical Atmospheres

See abstract on p. 160.

### Determination of Cobalt in Nickel and Nickel-containing Steels

B.I.S.R.A. METHODS OF ANALYSIS COMMITTEE: 'The Determination of Trace Amounts of Cobalt in Iron and Steel and Some Associated Materials.'
*Jnl. Iron and Steel Inst.*, 1959, vol. 191, Mar., pp. 236–40.

In certain atomic energy applications the cobalt content of the steels used is limited by specification to a maximum of 0·02, and even 0·01, per cent. Since none of the conventional analytical techniques is sufficiently sensitive for accurate determination of the metal in such trace amounts, work was undertaken to develop a process suitable for this purpose and also applicable to analysis of steelmaking materials, ores, ferro-alloys, etc. The exploratory studies are described in this paper and full details of the technique finally evolved are given in an appendix.

The method is based on photometric measurement of the cobalt complex with nitroso-R salt, after a zinc-oxide separation and precipitation of the cobalt with α nitroso β naphthol together with iron as 'carrier'. The procedure is suitable for use in analysing iron, steel, iron ore, nickel, chromium, and the ferro-alloys of manganese, titanium, niobium and chromium. Results are reproducible to within ±0·001 per cent. up to 0·01 per cent. cobalt and ±0·002 per cent. up to 0·04 per cent. of the metal.

Among the results tabulated are specimen analyses of low-alloy nickel-chromium steel, 18–8 chromium-nickel stainless steel and Mond nickel. The method has been recommended for adoption as a British Standard.

### Cadmium Plating of High-Strength Steels

D. J. CASH and W. SCHEUERMAN: 'High-Strength Steel can be Cadmium Plated without Embrittlement.'
*Metal Progress*, 1959, vol. 75, Feb., pp. 90–3.

During the past few years a considerable amount of research has been carried out to develop methods of cadmium plating which will give surface protection without embrittling high-strength steel: see, for example, work referred to in *Nickel Bulletin*, 1958, vol. 31, No. 8, pp. 225–6; 1959, vol. 32, No. 1, p. 14, also papers abstracted on pp. 142–143 of this Bulletin.

This contribution to the literature describes a modified process evolved by Cleveland Pneumatic Industries, Inc., in association with firms in the American aircraft industry. Based on the general consensus of opinion that the hydrogen in the coating is a prime factor in causing embrittlement, and that even very small amounts of hydrogen can give rise to the defect, work was directed towards permitting escape of the gas from the coating. In accordance with this concept, the method provides for production of a relatively porous cadmium coating, through which the hydrogen will quickly and easily diffuse. This type of coating is secured by (1) elimination of brighteners from a standard cadmium-plating solution, (2) use of a finely dry-blasted surface on parts which are to be plated (this also obviates the need for cleaning operations during which hydrogen may be introduced into the metal), and (3) deposition of cadmium at an average current density of 70 amp./sq. ft. (7·5 amp./dm.²). After plating, the parts are baked for 23 hours, to secure removal of the hydrogen present. By the method used it has been found possible to deposit coatings 0·0003–0·0005 in. (0·0075–0·0125 mm.) thick which are found to have satisfactory properties. Works experience with the new method is described. Particular reference is made to the use of the process in plating high-strength aircraft steel of the nickel-chromium-molybdenum A.I.S.I. 4340 type. The article includes description of control specimens used for assessment of the condition of the plated steel.

## HEAT- AND CORROSION-RESISTING MATERIALS

### The 'Nimonic' Alloys

W. BETTERIDGE: 'The 'Nimonic' Alloys.'
Published by *Edward Arnold (Publishers), Ltd.*, London, 1959; 332 pp. Price £4.

The book is placed in perspective in the foreword by Dr. L. B. Pfeil. Alluding to the development of the gas turbine during the last war and the need, in this connexion, for creep-resisting materials, Dr. Pfeil comments:

'The search for materials which would satisfy these demands led to intensive work on the nickel-chromium system, culminating in the development of precipitation-hardenable alloys of the 'Nimonic' series. Numerous variants, containing balanced

amounts and combinations of many modifying elements, have since been developed, but all these alloys owe their genesis to the binary 80–20 nickel–chromium alloy, from which they derive their fundamental characteristics.

'In the war years the nature of the specification requirements, and the urgency for their satisfaction, necessitated a more or less empirical approach to development of the properties called for: moreover, only over a long period has it been possible to establish, on a sound basis, the long-term creep properties of the respective alloys under varying conditions of temperature and stress. It has until now been deemed inadvisable to summarize information on the alloys, since data so assembled would rapidly have been superseded by results of later research, but the fund of knowledge and experience now accumulated warrants, at this stage, a comprehensive review.'

The information incorporated in the book is based on results of experimental investigation, supplemented by works' experience: it is presented in a form designed to be of service to all who have interest in high-temperature materials, whether from the point of view of their constitution and properties, or in relation to their use in the widening field of high-temperature engineering.

Some indication of the scope of the work may be derived from the contents list given below.

*Requirements of High-Temperature Alloys*
Creep of metals; aircraft jet-engine requirements; early work on nickel-chromium alloys.

*The Range of the 'Nimonic' Series*
Nomenclature; specifications and composition; creep criteria; forms available.

*Constitution*
Constitutional diagrams of the relevant basic alloy systems; structures of the 'Nimonic' alloys.

*Analysis and Identification*
Chemical and spectrographic methods; qualitative identification; gas content.

*Hot- and Cold-working*

*Heat-Treatment*
Annealing and precipitation-hardening treatments; influence of heat-treatment on creep and rupture properties; practical aspects of heat-treatment.

*Physical Properties*
Density; thermal expansion; specific heat; thermal conductivity; electrical resistivity; emissivity.

*Mechanical Properties at Normal Temperature*
Tensile and torsional properties; compressive strength; impact properties; frictional characteristics.

*Mechanical Properties at Elevated Temperatures*
Short-time tensile properties; creep and stress-rupture properties; fatigue; relaxation; thermal fatigue.

*Corrosion-Resistance*
Oxidation; sulphur attack; corrosion by fuel ash; corrosion by carbon; corrosion in other atmospheres; attack by molten metals.

*Joining*
Factors controlling the choice of a joining process; soldering; low- and high-temperature brazing; welding.

*'Nimonic' Alloys as Castings*
Compositions of casting alloys; melting and casting procedures; properties of 'Nimocast' alloys.

*Machining and Finishing*
Including reference to all relevant methods of mechanical machining, to flame-cutting, and to electro-machining.

*Inspection Methods*
Surface inspection; non-destructive testing for internal defects.

*Applications*
Gas turbines; ram-jet units; internal-combustion engines; heat-treatment and furnace components; metal-melting and -working equipment; high-temperature springs, etc.; future potential applications.

## Influence of Composition on High-Temperature Properties of Nickel-Molybdenum-Chromium-Iron Alloys

T. K. ROCHE: 'Influence of Composition upon the 1500°F. Creep Strength and Microstructure of Molybdenum–Chromium–Iron–Nickel-base Alloys.' *Oak Ridge Nat. Laboratory, Report ORNL* 2524, undated; 110 pp.

Results of research at Oak Ridge National Laboratory have shown that an alloy containing molybdenum 15–17, chromium 6–8, iron 4–6, carbon 0·04–0·08, per cent., balance nickel has properties indicating its suitability for use as a structural material in nuclear-power reactors. Some account of this work was given in *Nickel Bulletin*, 1959, vol. 32, No. 3, p. 85.

*Report 2524* gives details of further study of alloys within that range of composition, to determine the influence of the individual elements present. All the alloys investigated were within the following range of composition: molybdenum 10–20, chromium 5–10, iron 4–10, aluminium 0·5, manganese 0·5, carbon 0·06, per cent., balance nickel. They were tested in creep-rupture at a stress of 10,000 p.s.i. (4.45 t.s.i.; 7 kg./mm.$^2$), all being subjected to test in the annealed condition. The criterion used to evaluate was the time required to reach strains between 1 and 10 per cent. A general consideration of the detailed data reported supports the specification proposed for the 'INOR 8' alloy developed at Oak Ridge: see *Nickel Bulletin, loc. cit.*

### Compressive, Bearing and Shear Creep-Rupture Properties at Elevated Temperatures

L. A. YERKOVICH: 'Investigation of the Compressive, Bearing and Shear Creep-Rupture Properties of Aircraft Structural Metals and Joints at Elevated Temperatures.'

*Wright Air Development Center, Tech. Report* 54–270, May 1958; 115 pp.

In the assembly of structural members of aircraft, rivets and other mechanical fasteners are usually required to carry and to transmit loads. The ability of joined members to sustain loads which may be imposed on them is therefore frequently dependent on the strength characteristics of the element which forms the joint, and, in some cases, upon the stress condition created in the joint area. In spite of the complicated stress patterns set up when loads are transmitted through joints, determinations of shear and bearing characteristics of joints have provided guidance adequate to permit satisfactory design for components working within the range of temperature in which the effects of creep are not encountered. High-speed flight has, however, changed the situation, and it has become apparent that certain values hitherto used for design are not valid under the more severe conditions of service.

This report deals with a research sponsored at the Wright Air Development Center, to determine the creep behaviour of some aircraft structural materials under the influence of shear, bearing and compressive stresses. Fifteen materials were tested in sheet and/or plate and/or bar form, and the results of the tests were correlated with the tensile-creep and -rupture characteristics of the respective alloys. The materials selected as typical of those having interest in connexion with structures used in high-speed flight were two aluminium alloys, four titanium-base alloys, a low-chromium steel, 'Monel', and six austenitic steels, of simple and complex types.

The test temperatures varied, according to the nature of the alloys, through ranges which for the aluminium alloys were 350°–600°F. (176°–315°C.), to temperatures of the order of 1000°–1350° or 1500°F. (538°–732° or 815°C.) for the austenitic steels.

From the very large amount of experimental data recorded, the general conclusion reached is that the creep properties under compression, bearing and shear stresses are closely similar to those characteristic of the respective materials in tensile creep.

### Structure of Precipitation-Hardening Nickel-base High-Temperature Alloys

W. C. BIGELOW and J. A. AMY: 'Electron-Metallographic Studies of Nickel-base Heat-Resistant Alloys.'

*Wright Air Development Center, Report No.* 58–406, Aug. 1958; 49 pp.

Nickel-chromium–(cobalt)-base alloys of the age-hardenable types containing titanium and aluminium are recognized as an outstandingly important group in the high-temperature field. Many materials of that type, varying in the proportions of other elements present, have been developed, and have proved their value in components of gas turbines and other parts working under conditions of stress, further complicated, in many cases, by atmospheres involving corrosion and oxidation attack.

It is generally accepted that the high strength of these alloys is related to a precipitation reaction which occurs on ageing (after suitable solution treatment) at temperatures above 1200°F. (650°C.). This reaction, resulting from the presence of titanium and aluminium, involves formation of the intermetallic $\gamma'$ phase, which is structurally similar to the $Ni_3Al$ phase of the nickel-aluminium system. Considerable research has recently been carried out to determine the mode of precipitation of the hardening phase, and to establish the relationships between the distribution of that phase and the properties of the alloys. In this work electron-microscope techniques have proved particularly useful because, at the stage at which the particles of the phase exert their maximum influence, they are usually too small to be revealed by the optical microscope.

This report describes research planned with the dual purpose of developing procedures for studying the nickel-base alloys by electron microscopy, and of applying these techniques to the study of individual alloys. In the first section a detailed and well-illustrated account is given of polishing and etching procedures suitable for these alloys, and of the preparation of surface replicas and extraction replicas. The second section, opening with a concise discussion of the characteristics of the $\gamma'$ phase, reports examination, by the methods described, of precipitation phenomena characteristic of four typical nickel-base precipitation-hardening alloys: for compositions, see Table I, p. 154.

The thermal treatments applied to the respective alloys are shown in Table II, p. 154.

Specimens about $\frac{3}{8}$-in. (10-mm.) thick were taken from $\frac{3}{4}$-in. (19-mm.) square rolled bar stock and were solution-treated as indicated in Table II. One specimen of each alloy was allowed to cool in air after the solution treatment; the remainder were rapidly quenched by immersion in a saturated ice-brine bath. These latter specimens were then aged, as shown in the table, and air-cooled to room temperature. Hardness variations were correlated with precipitation of the $\gamma'$ phase: possible mechanisms contributing to these variations are discussed.

Since examination of these alloys had shown that the microstructures and hardness depend fundamentally on their titanium and aluminium contents, supplementary examination was made of an alloy, designated '1079', closely similar in type to 'Udimet-500', but having higher titanium and aluminium contents: nickel 51·7, chromium 19·0, cobalt 16·8, molybdenum 3·7, titanium 4·1, aluminium 4·1, manganese 0·1, silicon 0·3, carbon 0·06, per cent.

Further studies were made on a cast nickel-base alloy typical of materials used for production of

**Table I**

| | Ni* % | Cr % | Co % | Mo % | Fe % | Al % | Ti % | Nb % | Mn % | Si % | C % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 'Inconel-X' | 73·3 | 14·9 | — | — | 6·59 | 0·78 | 2·38 | 1·02 | 0·56 | 0·38 | 0·04 |
| 'Waspaloy' | 56·6 | 19·5 | 13·4 | 2·8 | 2·90 | 1·09 | 2·20 | — | 0·88 | 0·62 | 0·09 |
| 'M-252' | 52·8 | 18·9 | 11·3 | 9·4 | 1·63 | 1·14 | 2·88 | — | 1·28 | 0·59 | 0·12 |
| 'Udimet-500' | 52·4 | 20·0 | 16·7 | 3·9 | — | 3·36 | 3·15 | — | 0·10 | 0·10 | 0·08 |

* by difference

**Table II**

| | 'Inconel-X' | 'Waspaloy' | 'M-252' | 'Udimet-500' |
|---|---|---|---|---|
| Solution Treatments | 2 hr. at 2050°F. (1120°C.) | 4 hr. at 1975°F. (1080°C.) | 4 hr. at 1975°F. (1080°C.) | 4 hr. at 1975°F. (1080°C.) |
| 1400°F. (760°C.) Ageing Treatments** | 1, 10, 100, 1000 hr. | 10, 100 hr. | 10, 100 hr. | 10, 20, 40, 100, 1000 hr. |
| 1600°F. (870°C.) Ageing Treatments** | 1, 10, 100, 1000 hr. | — | — | 1, 4, 10, 40 hr. |

** After ice-brine quenching from solution treatment

turbine blades and other precision parts for aero engines. That material ('Guy Alloy') was of the following composition: nickel 67·9, chromium 13, iron 4·5, aluminium 6·0, carbon 0·1, boron 0·5, niobium 2·0, per cent. In view of the known influence of production methods on casting alloys of this type, specimens from vacuum- and air-melted heats were examined, in the as-cast condition and after rupture testing at 1500°F. (815°C.). Finally, the research was extended to cover examination of banded structure in an experimental alloy containing carbon 0·3, titanium 3·0, aluminium 3·0, molybdenum 3·5, chromium 19·5, cobalt 14·5, per cent., balance nickel. The alloy was solution-treated at 1975°F. (1080°C.) for 4 hours, water-quenched, and aged for 10 hours at 1400°F. (760°C.).

Much detailed information, illustrated by numerous electron micrographs, is given in the report. The following main general conclusions are drawn:

The work demonstrated afresh the value of electron microscopy in study of precipitation phenomena.

With regard to the mode of precipitation and the nature of the precipitate, the following observations are made:

'A very large number of $\gamma'$ particles was observed in all the alloys when aged at 1400° or 1600°F. (760° or 870°C.). The size of the particles generally increased with the period and temperature of ageing, and their number increased with the titanium and aluminium content of the alloys. The particles were usually spherical in form and were uniformly distributed, in a random pattern, through the matrix grains of the alloys. Cuboidal particles, having preferred orientations and alignment, were observed in a few specimens of the 'Inconel-X' and '1079' alloys. The $\gamma'$ phase in the four commercial alloys (see Table I) had an ordered f.c.c. crystal structure similar to that reported for that phase in simpler alloys, and all particles in a given matrix grain showed a common crystallographic orientation.

'Although the volume per cent. of the $\gamma'$ phase increases with the titanium and aluminium content of the alloys, it appears that the composition of this phase in the complex commercial alloys does not correspond to the formulae $Ni_3Al$ and $Ni_3(Al, Ti)$ which are frequently used to represent it. This conclusion is reached because the maximum volume per cent. of the phase observed was greater than would be expected from the titanium and aluminium content of the alloys, assuming that these formulae were applicable. It is therefore concluded that in the commercial types of alloy elements other than titanium substitute for aluminium in the basic $Ni_3Al$ structure, to form the $\gamma'$ phase. Results of spectrographic analysis, combined with the observation that there is a decrease in the volume per cent. of the phase during isothermal ageing, suggest that the amount of these elements incorporated is greatest in the early stages of ageing, and that a refinement of composition accompanies the agglomeration and growth of the particles as ageing is prolonged. Qualitative spectroscopic analysis indicated the presence of rather large amounts of cobalt, chromium and niobium in the $\gamma'$ phase of alloys containing those elements. In contrast, only traces of molybdenum were detected in the $\gamma'$ phase precipitated in alloys containing relatively large amounts of that element.

'The age-hardening of the alloys was definitely

found to be associated with the development of $\gamma'$ particles of size sufficiently large to be detectable with the electron microscope. The overall hardening process appears, however, to be a complex one, to which several mechanisms contribute. When solution-treated and quenched so as to eliminate detectable particles of $\gamma'$ phase, all the alloys exhibited minimum hardness. A few hours of ageing at 1400° or 1600°F. (760° or 870°C.) caused development of a fine dispersion of $\gamma'$ particles, accompanied by large increase in hardness, which is attributed both to dispersion effects resulting from the presence of the numerous particles of precipitate and to strains generated by coherency between the particles and the matrix. The hardness of all the alloys except 'Inconel-X' remained relatively constant with further ageing for periods of 100 hours at 1400°F. (760°C.), indicating that at that temperature the particles remained coherent and retained favourable dispersion for long periods. Ageing 'Inconel-X' at 1400°F. (760°C.) and ageing all the alloys at 1600°F. (870°C.) caused marked fall in hardness after about 10 hours, an effect attributed to loss in coherency. The fact that the hardness of the alloys, when comparably aged, usually increased with Ti + Al content appeared to be due primarily to dispersion effects resulting from the accompanying increase in the number of $\gamma'$ particles present.

'No variations in size, shape or distribution of the $\gamma'$ particles could be found which would account for the fact that vacuum melting and the addition of small amounts of boron and zirconium markedly increase the high-temperature rupture life of nickel-base alloys of the types examined. It would appear that these factors influence the characteristics of the grain-boundary precipitates, thus affecting rate of development of intergranular cracking.

'The low creep strength associated with banded structure in some experimental alloys is believed to be due to a weakness of the matrix grains, resulting from an uneven distribution and over-aged condition of the precipitate particles. The irregular distribution in restricted bands probably results from non-uniform distribution of the titanium and aluminium through the alloy, due to unsuitable melting or pouring conditions, from solution-treating at too low a temperature, or from strain-induced precipitation due to too low a rolling temperature. The defect can be eliminated by correct control of processing conditions.

'Observations made on the cast alloy show that the microstructures of cast alloys of this type may differ considerably from those found in wrought materials of comparable composition and that under the influence of stress and high temperature drastic microstructural changes may occur in the cast materials.'

**Nickel-Chromium Precipitation-Hardenable Steel: 'Unitemp 212'**

'High Strength at 1400°F. Claimed for Precipitation-Hardening Steel.'

*Materials in Design Engineering*, 1959, vol. 49, Jan., pp. 120, 122 and 124.

A new precipitation-hardenable austenitic steel, developed by Universal Cyclops Steel Corporation and designated 'Unitemp 212', is claimed to maintain high strength and oxidation-resistance at temperatures up to 1400°F. (760°C.). The properties and working characteristics of the steel (the composition of which is shown in the table below) are outlined in the article, together with notes on availability and heat-treatments.

A solution-treatment at 1800°F. (980°C.) is recommended for an optimum combination of properties, though higher solution-treatment temperatures may be used to improve rupture strength at 1350°F. (735°C.), with, however, some sacrifice in notch-rupture properties at 1200°F. (648°C.). Ageing is effected at 1375°F. or 1325°F. (745°C. or 717°C.), depending on the properties required. Details are given of the five heat-treatments used to obtain the various combinations of mechanical properties referred to in the tables and curves included in the article.

Values for short-time tensile properties in the aged condition are plotted against temperature, and tabular data indicate typical minimum tensile properties at room temperature, 1000°, 1200° and 1400°F. (538°, 648° and 760°C.). The suitability of the steel for use, in bar and sheet form, in sub-zero applications is illustrated by data on tensile properties at −320°F. (−196°C.). Oxidation-resistance at temperatures up to 1800°F. (981°C.) is similar to that of the A.I.S.I. Type 302 chromium-nickel stainless steels.

'Unitemp 212' is easily machined and welded and its formability is stated to be good. The steel may be melted either in air or by specialized processes designated respectively, 'Duomelt', 'Inductovac', and 'Duovac'.* Notes on availability are included in the article.

* No details are given of these techniques.

**Composition of 'Unitemp 212' Steel**

| C % | Si % | Mn % | S % | P % | Ni % | Cr % | Ti % | Al % | Nb+Ta % | B % | Zr % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·05-0·15 | 0·50 max. | 0·50 max. | 0·04 max. | 0·04 max. | 23-27 | 15-17 | 3·70-4·30 | 0·50 max. | 0·30-0·90 | 0·005-0·10 | 0·02-0·09 |

**Vacuum-Induction Melting**

See abstract on p. 138.

**Resistance of High-Temperature Materials to Attack by Boron Oxide**

D. ROLLER and C. R. ANDREWS: 'Effect of Molten Boron Oxide on Selected High-Temperature Alloys.' *Corrosion*, 1959, vol. 15, Feb., pp. 85t-96t.

Considerable interest has arisen during recent years in boron and boron-containing compounds, in both civil and military applications. *Inter alia*, there is a wide and expanding market for such materials in borosilicate glasses, glass fibres, ceramics, high-temperature alloys, and certain organic intermediates. This increasing use of boron oxide has resulted in a demand for more precise and complete knowledge of its characteristics, and the research described in this paper is a contribution towards assembly of such information.

The paper opens with a discussion of the various oxides of boron, the most stable of which is $B_2O_3$ (also designated boric acid anhydride or boric oxide), which exists in an amorphous state, in vitreous form, or in a crystalline state, depending on temperature and on water content. The $B_2O_3$ oxide only is dealt with in this paper, since it is of greatest practical interest: the characteristic properties of the compound, in the three forms mentioned, are described. It is noted, as relevant to the investigation reported, that molten boron oxide is acidic in nature and is a strong flux, by which many compounds, especially oxides, are attacked. It was therefore to be anticipated that the compound would be corrosive to high-temperature materials which rely for protection upon the formation of oxide films or scales. The authors give reference to previous work on this subject, which had shown that molten boron oxide can attack many alloys at temperatures above 1700°F. (925°C.), and that above 2000°F. (1095°C.) it attacks almost all metallic materials. Earlier experiments have shown that corrosion is particularly severe under intermittent-immersion conditions.

The programme for the investigation now reported included design and construction of a high-temperature test furnace, in which provision could be made for establishment of the varying conditions to be covered. (The set-up is described and illustrated.)

The influence of the following factors was evaluated: temperature, composition of alloy, atmosphere (liquid or gaseous), rate of immersion cycling, degree of immersion of the specimens in the molten boron oxide. Other variables considered were the effect of water vapour, stress (both cyclic and constant) and the effect of addition agents in the boron oxide. End-use applications known and envisaged indicated the desirability of test periods of the order of 150 hours, and of determining the effect of exposure to boron oxide on the mechanical properties of the alloys. Test temperatures ranged from 1600° to 2150°F. (871° to 1177°C.).

The materials selected for study (see table on p. 157) were representative of high-temperature alloys of iron, nickel and cobalt base and of other types known to have important high-temperature applications. The nature of the respective alloys, and the considerations dictating their selection, are discussed.

The methods used to evaluate the effect of exposure to the corroding medium were:

(1) Microstructural examination.

(2) Determination of room-temperature tensile, yield and elongation values, before and after exposure.

(3) Spectrographic examination of the surface scale formed on the test materials and of the boron oxide remaining in the test crucibles after test.

The results are presented in detail, for each alloy of the test series, and some additional observations are recorded with regard to the effects of the boron-oxide environment on certain components of the test apparatus, including 'Chromel'/'Alumel' thermocouples used in the test chamber, and an 'Inconel' tube which supported the specimens in the furnace. The report is illustrated by numerous photomicrographs of typical specimens after exposure under varying conditions.

Consideration of the observed effect of the composition of the alloys is linked with discussion of previously published data on the solubility of various oxides in molten boron oxide, and the information obtained from both sources is used to form a basis for a proposed mechanism of attack by boron oxide.

The results demonstrate that at temperatures above 1800°F. (980°C.) molten boron oxide can, within 150 hours, seriously corrode unstressed specimens of the high-temperature alloys tested. The attack is specially severe on iron- and cobalt-base alloys and on materials containing appreciable quantities of aluminium and/or titanium, e.g., 'Alumel' was more severely attacked than 'Chromel'. Of the materials tested, 'Inconel' was the most resistant. Nickel, molybdenum and probably chromium are unaffected by molten boron oxide, indicating that these metals might be useful as protective coatings.

Tensile strength and elongation are highly sensitive criteria of the damage resulting from exposure to boron oxide. Yield strength is not seriously affected in the initial stages of exposure, at which stage the plastic properties rather than the elastic characteristics undergo deterioration.

Intergranular attack, surface oxidation, and pitting attack (both surface and sub-surface) occur when molten boron oxide comes into contact with the alloys in an air atmosphere, and the formation of some new phases was also encountered.

Information available to date suggests three possible mechanisms to explain the nature of the boron-oxide attack: (1) excessive oxidation, which promotes interface attack at the boron-oxide/air/metal interface, by fluxing and solution of metal oxides, (2) intergranular attack by diffusion and/or preferential leaching of certain alloy constituents, and (3) reduction of molten boron oxide by certain alloy constituents (including aluminium and titanium), resulting

**Composition of Test Alloys**

(*See abstract on p. 156*)

| Elements % | Alloy | | | | | | |
|---|---|---|---|---|---|---|---|
| | 'Stellite 25' | 'R-235' | 'Multimet N-155' | 'Inco 702' | 'Nimonic 75' | 'Inconel' | A.I.S.I. Steel Type 310 |
| Cr | 20·10 | 14·98 | 21·88 | 16·53 | 20·44 | 15·5 | 24·0-26·0 |
| W | 15·15 | — | 2·44 | — | — | — | — |
| Fe | 1·72 | 9·80 | 29·96 | 0·44 | 0·78 | 7·0 | Bal. |
| C | 0·09 | 0·12 | 0·10 | 0·04 | 0·14 | 0·04 | 0·25 max. |
| Si | 0·43 | 0·13 | 0·57 | 0·22 | 0·57 | 0·20 | 1·50 max. |
| Co | 51·16 | 0·21 | 19·55 | — | — | — | — |
| Ni | 9·86 | 64·77 | 19·75 | 78·9 | 77·03 | 76 | 19·0-22·0 |
| Mn | 1·42 | 0·03 | 1·66 | 0·06 | 0·45 | 0·35 | 2·00 max. |
| Nb, Ta | — | — | 0·97 | — | — | — | — |
| Mo | — | 5·16 | 2·97 | — | — | — | — |
| $N_2$ | — | — | 0·12 | — | — | — | — |
| P | 0·012 | 0·001 | 0·016 | — | — | — | 0·040 |
| S | 0·009 | 0·011 | 0·012 | 0·007 | 0·007 | — | 0·030 |
| Ti | — | 2·60 | — | 0·73 | 0·36 | — | — |
| Cu | — | — | — | 0·10 | 0·04 | — | — |
| Al | — | 2·19 | — | 2·95 | 0·16 | — | — |

in formation of elemental boron, which diffuses into the alloy, forming new phases characterized by low oxidation-resistance, or by low-melting eutectics.

The static tests showed that unstressed high-temperature alloys are not seriously affected by boron-oxide/air environments at 1800°F. (980°C.) within 150-hour periods, and in unstressed static tests 'Inconel' showed excellent resistance, under such conditions, up to about 2000°F. (1095°C.).

## Oxidation of Chromium-Nickel Steels

D. CAPLAN and M. COHEN: 'High-Temperature Oxidation of Chromium-Nickel Steels.'

*Corrosion*, 1959, vol. 15, Mar., pp. 141t-6t.

In 1952 the authors published a report on the scaling of three chromium steels (*Jnl. of Metals*, vol. 4, pp. 1057-65). In that work the principal finding was that breaks in the weight-gain/time curves could be related to the accumulation of silica as a separate phase at the metal/scale interface. Periods of accelerated oxidation resulted from cracking of the protective scale after a layer of silica had isolated it from the metal. The work now reported, which is an extension of that research, is concerned with observation of the oxidation characteristics of four steels of the types shown in the table shown on p. 158.

As in the earlier experiments, weight-increase of the specimens was followed as a function of time of exposure at various temperatures. Scales removed from the specimens were examined microscopically and by X-ray diffraction and were colorimetrically and spectrographically analysed.

Most of the specimens were machined, emery polished, and finished by electropolishing: some were only scrubbed and degreased after being emery-abraded. Test temperatures were 1600°, 1800° and 2000 °F. (871°, 982° and 1093°C.). The prepared atmospheres were dry air or air saturated with moisture at 90°F. (32°C.), flowing upwards, in a vertical tube furnace, at 200 ml./min.

Nearly all the oxidation/time curves exhibit one or more breaks, indicating that the abrupt changes in rate of scaling observed with the chromium steels extend to stainless steels in general, and the accumulation of silica at the metal/scale interface, previously observed on the straight-chromium steels, was found to occur also with the austenitic types. Two types of break were observed. Type I break marks the end of an initial period of intensive protection

**Composition of Stainless Steels used in Oxidation Experiments**

(*See abstract on p. 157*)

| Steels | C % | Si % | Mn % | Ni % | Cr % |
|---|---|---|---|---|---|
| A.I.S.I. Type 302 (two specimens) .. | 0·11 | 0·59 | 0·34 | 8·3 | 19·0 |
| Type 302 (seven specimens) .. | 0·07 | 0·40 | 1·49 | 10·1 | 18·7 |
| Type 330 .. .. .. | 0·06 | 0·65 | 1·66 | 35·0 | 14·3 |
| Type 309 .. .. .. | 0·12 | 0·63 | 1·90 | 13·2 | 23·0 |

due to a thin film of high chromium content (and perhaps also high silicon), which is formed during the prior treatment given to the specimens. (The nature of the reactions set up by various pre-treatments, as influencing the breakdown of the protection, is discussed, with emphasis on the need for ensuring, on materials which are to be subjected to corrosive conditions at high temperatures, as innocuous a film as possible.) The Type II break occurs after a relatively thick protective scale has formed. Isolation of the scale from the metal, by accumulation of silica and occurrence of voids at the metal/scale interface, followed by cracking of the scale as a result of recrystallization, exposes the metal surface to the oxidizing gas.

The tendency to growth of wart-like formations during oxidation is not yet understood; the authors make some suggestions as to the possible cause of the warts and the nature of their growth.

The presence of moisture in the air was found to accelerate scaling of the nickel-chromium steels. (With the straight-chromium steels the presence of moisture had in some cases increased, in others decreased the rate of scaling.) No theory adequate to explain the influence of moisture has yet been developed.

The authors consider that two factors call for further investigation in connexion with scaling tests: (1) methods of surface preparation of the specimens, and (2) closer control of variables introduced by the minor constituents present in many materials used at high temperatures.

### Oxidation-Resistant Coatings for Molybdenum

J. R. BLANCHARD: 'Oxidation-Resistant Coatings for Molybdenum.'

*Wright Air Development Center, Report* 54-492; 56 pp.; Dec. 1954; recently de-classified.

The 'catastrophic oxidation' to which molybdenum and molybdenum-base alloys are subject at temperatures above 1200°F. (650°C.) has led to considerable research on methods which could give protection, thus permitting advantage to be taken of the valuable high-temperature strength of the metal.

The following methods have been investigated in the course of research in the U.S.A., the U.K., and other countries: cladding; immersion in molten-metal baths; cementation; deposition of coatings from the vapour phase; coating with ceramics; metallizing (metal spraying).

The report to which this abstract relates is concerned with work sponsored by Wright Air Development Center, at the laboratories of Climax Molybdenum Company. It covers results obtained and observations made during four years' research in which the main attention was devoted to protection by metallizing. Improved methods of application of the protective media, and of testing the treated material, were gradually evolved, and this summary has been prepared to constitute a basis for further development. Details are given of methods of coating (including diffusion treatments): tests used for evaluation of the coated specimens (oxidation, thermal-cycling, thermal-shock, and ductility tests, and examination of surface finish); character of the coating materials used; metallographic examination.

The twelve materials shown below (applied by metallizing) were found to show promise as protective coatings, the criterion being that panels so coated showed no oxidation of the basis metal after exposure in flowing air at 1700° and 1800°F. (927° and 982°C.) for 500 hours.

Cr-Si alloy
Cr-Mo-Si alloy
Fe-Si alloy
Ni-Si alloy
Si-Fe-Cu-Mg alloy
Fe-Cr-Si alloy
Mo-Ni-Si alloy
Two aluminium alloys
Si+Al powder mixtures
'Colmonoy No. 5' } Ni-Cr-B-Si-Fe
'Colmonoy No. 6' } alloys

Specimens coated with Al-Cr-Si and with 'Colmonoy 5' which showed particular promise, were subjected to additional oxidation tests, at 2000°F. (1093°C).

Oxidation tests on molybdenum specimens electroplated with chromium showed that some protection can be so obtained if plating conditions are suitably controlled. Electrodeposited nickel coatings were less resistant to oxidation and nickel+chromium coatings were also inferior to chromium.

### Diffusion and Oxidation of Metals: Literature Reviews

See abstract on p. 138.

**Growth and Scaling Tests on Cast Irons**

See abstract on p. 150.

**Determination of Proof Stress of Steel at Elevated Temperatures**

See abstract on p. 138.

**Use of 'Inconel X' in High-Speed Research Aircraft**

N. WOOD: ' 'X-15' Space Plane Tribute to Engineering, Materials Ingenuity, 'Inconel' Fabrication.'

*Reprint* from *Western Metalworking*, 1958, Nov.
Issued by INTERNATIONAL NICKEL CO., INC., 1959; 3 pp.

The article contains notes on the use of the nickel-chromium-base age-hardenable alloy 'Inconel X' in the 'X-15', the manned space-research aircraft developed by North American Aviation, Inc. It was known that during high-speed, high-altitude flight the aircraft would be subjected to extremes of temperature, ranging from 1200° to −300°F. (650° to −185°C.), occurring almost simultaneously in various sections of the structure. The high creep strength of 'Inconel X', its resistance to thermal fatigue and its good impact and notch strength at the sub-zero temperatures involved, allied with the substantial experience which had been accumulated in production and fabrication of the alloy, dictated its final choice as the main structural material.

Hitherto use of 'Inconel X' in airframes had been limited to a few parts in the vicinity of jet engines where service temperatures were above 800°F. (425°C.). Its application as an aircraft-skin material (for which it was used for the first time in the 'X-15') is expected to increase with rise in service temperatures. Brief reference is made in the article to some of the methods developed to overcome problems encountered in fabrication and welding of the Inconel X' components.

*See also*

R. R. FERGUSON: 'Making of Aircraft Structures from 'Inconel X'.'

*Reprint* from *Amer. Soc. Tool Engineers, Tech. Paper No.* 178, vol. 58, Book 2.
Issued by INTERNATIONAL NICKEL COMPANY, INC., 1959; 11 pp.

The author is a research engineer with North American Aviation, Inc. The paper discusses the procedures used by that Company for heat-treating, welding, machining, forming and cleaning 'Inconel X', during the construction of a 'high-speed research-type aircraft' in which the alloy was employed as the main material of construction (*inter alia*, for welded tanks 6 ft. (1·8 m.) in diameter and 12 ft. (3·6 m.) long, sculptured wing skins, and complex beam structures).

Details of heat-treatment are given in sections concerned, respectively, with solution-treatment, ageing, stress-relief treatment after forming and welding and before ageing, annealing treatment for softening prior to forming and welding, warpage during heat-treatment, and removal of oxide films from parts which, because of their size, have to be heat-treated in an air atmosphere. Textual information is supplemented by graphical data indicating the influence of heat-treatment variables on the properties obtained.

It is usually recommended that 'Inconel X' should not be welded at a hardness higher than 25 Rockwell C, because above that hardness level ductility would be insufficient to relieve the stresses resulting from weld shrinkage or prior working. The procedure used to achieve the condition required for welding is discussed and brief notes are given on fusion and resistance welding. Machining is considered under the heads of milling, 'chem-milling'*, and flame-cutting, and procedures used to clean 'Inconel X' before heat-treatment are also described. In the last section of the paper some welded parts made in 'Inconel X' are illustrated.

**Influence of Heat-Treatment on Properties of Corrosion-Resisting Nickel-Molybdenum-Iron Alloys**

K. BUNGARDT and H.-H. WEIGAND: 'Influence of Heat-Treatment on Properties of Corrosion-Resisting Nickel-Molybdenum Alloys.'

*Zeitsch. f. Metallkunde*, 1959, vol. 50, Jan., pp. 11–18.

Optimum properties in the corrosion-resisting nickel-molybdenum-base alloys containing up to 30 per cent. molybdenum are obtained by solution-treatment followed by quenching to ensure retention in solution of the maximum amount of molybdenum. Subsequent exposure of the alloys to a high temperature (as, for example, in high-temperature service or during welding) induces precipitation from the supersaturated solid solution, which can considerably influence the mechanical and corrosion-resisting characteristics. The work described in the paper was carried out on four nickel-molybdenum-base alloys (see table, p. 160) to determine the effects, on microstructure, hardness, tensile properties and corrosion-resistance, of heating in the precipitation range (about 500°–1200°C.).

Specimens were solution-treated according to the procedures customarily used for the individual alloys, but, in supplementary tests to study the influence of the solution-treatment temperature, alloy 3 was also quenched from temperatures in the range 1175°–1250°C. After microscopical examination to determine that no secondary precipitation had occurred, the specimens were exposed to temperatures in the precipitation range for periods of 2 minutes to 25 hours, and, in a few cases, up to 1000 hours. (For times longer than 1 hour the alloys were exposed in an argon atmosphere.) The specimens were then subjected to metallographic examination and hardness, tensile and corrosion

* A process developed by North American Aviation, Inc. specifically for machining 'Inconel X'. In chem-milling metal is removed at the rate of about 0·001 in. per minute (0·025 mm. per minute): the thickness tolerance is ±0·002 in. (0·05 mm.) over the original thickness tolerance and the surface roughness is about 100 rms. A chem-milled part is illustrated in this paper.

**Composition of Nickel-Molybdenum-base Alloys used for Corrosion Tests**

(*See abstract on p. 159*)

| Alloy | C % | Si % | Mn % | Cr % | Mo % | Ni % | Fe % | Ta/Nb % |
|---|---|---|---|---|---|---|---|---|
| 1 | 0·02 | 0·34 | 1·02 | — | 21·11 | 56·8 | 19·6 | — |
| 2 | 0·02 | 0·05 | 0·43 | — | 29·38 | 63·19 | 6·88 | — |
| 3 | 0·02 | 0·44 | 1·01 | 17·46 | 16·9 | 58·64 | 5·22 | — |
| 4 | 0·02 | 0·98 | 1·4 | 21·14 | 6·05 | 46·00 | 20·17 | 2·23 |

tests. Corrosion-resistance was determined by exposure to the following media:

Alloy No. 1 10% boiling HCl
„ „ 2 21% „ „
„ „ 3 1% and 10% boiling HCl
„ „ 4 10% $H_2SO_4$

Alloy 3 was tested also in an oxidizing medium (20 per cent. $H_2SO_4+KNO_3$ at boiling temperature). The results of the investigation are discussed in detail.

It was found that after heating in the range 700°–1100°C. precipitation occurred in all the alloys, the precipitates forming a continuous band along the grain boundaries and coagulating after prolonged heating. In the chromium-free alloy No. 2 two intermetallic phases also were distinguished after long-time heating.

Pronounced increase in hardness occurred only when large amounts of precipitate were present in the microstructure; use of higher solution-treatment temperatures had the effect of lowering the hardness achieved by heating in the precipitation range. Reduction in area and elongation at rupture decreased considerably, and yield point and tensile strength increased slightly, as a result of precipitation treatment.

Corrosion-resistance was considerably influenced by the ageing treatment. Loss in weight of alloys 1 and 2 increased appreciably in the presence of grain-boundary precipitates, but the corrosion rate of alloy 2 increased only after long exposure at temperature (at which stage a new phase begins to form). Susceptibility to intergranular attack was induced in alloys 1, 2 and 3 after heating in the 600°–800°C. range, due to precipitation of a molybdenum-rich phase at the grain boundaries and resultant molybdenum impoverishment in the matrix. Increased loss-in-weight is to be expected as long as a molybdenum gradient exists between the precipitation region and the interior of the grain, and this tendency will be arrested only after long-time heating or exposure to an elevated temperature, to permit adequate diffusion of molybdenum from within the grain to the impoverished zone.

In the case of alloy 3 sensitization at 800°–900°C. also induces susceptibility to intergranular attack under oxidizing conditions; therefore, with this alloy, precipitation of a chromium-containing phase must also be taken into consideration.

## Corrosion of Metals in Marine Tropical Atmospheres

B. W. FORGESON, C. R. SOUTHWELL and A. L. ALEXANDER: 'Corrosion of Metals in Tropical Environments. Part III. Underwater Corrosion of Ten Structural Steels.'

*U.S. Naval Research Laboratory, Report N.R.L.* 5153, Aug. 8, 1958; 24 pp.

Since 1946 an extensive investigation has been in progress in the Panama Canal Zone, to determine the corrosion-resisting characteristics of fifty metals and alloys exposed to five tropical environments: marine and inland atmospheres, fresh-water immersion, and continuous and mean-tide sea-water conditions. Ten identical panels of each material have been exposed in each location, to permit removal of two panels from each site after one, two, four, eight or sixteen years. The background to the investigation and the conclusions drawn to date are outlined in abstracts of the two previous reports which appeared in *Nickel Bulletin*, 1958, vol. 31, No. 2, pp. 59–60; No. 9–10, pp. 272–3. The first report related to corrosion of aluminium, lead, copper, zinc, nickel and structural steel. Of the ten structural steels considered in the second report, four were proprietary high-strength low-alloy types (Cu-Ni, Cu-Cr-Si, Cu-Ni-Mn-Mo and Cr-Ni-Mn); one was a 2 per cent. nickel boiler steel; one was a 5 per cent. nickel steel; two were high-tensile chromium steels, and two were low-carbon steels (one copper-bearing). The present report is concerned with further evaluation of the corrosion characteristics of the same steels, during continuous immersion in fresh water, and continuous and mean-tide immersion in sea water.

The results, from which the following general conclusions are drawn, are presented in detail.

Corrosion of unalloyed low-carbon steel in tropical sea-water conditions was of the same magnitude as in temperate sea water at Kure Beach and was less than the corrosion suffered at Port Hueneme, California. The profuse marine growth on the panels in the Panama water probably afforded some protection.

There was little difference among the rates of corrosion of unalloyed low-carbon steel in the three environments in the Panama tests, but the shapes of the curves relating to these exposures indicated that sea-water corrosion was proceeding at a linear

rate, that fresh-water corrosion was steadily decreasing as time of exposure was prolonged, and that mean-tide corrosion was accelerating.

No significant difference in type or magnitude of corrosion was found between copper-bearing steel and unalloyed low-carbon steel in sea or fresh water and at mean-tide. Inclusion of 2 or 5 per cent. of nickel in structural steel did not increase its resistance to corrosion in fresh water or at mean-tide, and in sea water the nickel addition accelerated both loss of weight and pitting.

Addition of chromium (3 or 5 per cent.) to structural steel gave some improvement in fresh water, but in sea water some of the chromium steels showed frequent pitting.

Proprietary low-alloy steels were not in general more resistant to underwater corrosion than was the mild unalloyed carbon steel, and in certain conditions of exposure these steels were considerably less resistant.

The results confirmed the inadequacy of short-term tests as a measure of ultimate corrosion, and it is clear that since the corrosion/time curves were not linear and varied in shape with variation in environments, true rates of corrosion could not have been established with shorter exposure.

The conclusion drawn by other investigators that low alloy additions have no great value in increasing the corrosion-resistance of steels immersed in sea water was in most cases confirmed by the results of these tests, but the deleterious effects of some alloy elements, which developed after long periods of exposure in these tropical environments, were unexpected, and it is suggested that they should be carefully considered in relation to selection of structural steels for use in such conditions.

**Comparative Corrosion-Resistance of Chromium-Manganese-Nickel and Chromium-Nickel Austenitic Steels**

A. C. HAMSTEAD and L. S. VAN DELINDER: 'Comparative Corrosion-Resistance of 200 and 300 Series Stainless Steels in Chemical Manufacturing Processes.'
*Corrosion*, 1959, vol. 15, Mar., pp. 147t–55t; disc., pp. 155t–7t.

Although within a relatively short period much information on the properties of the high-manganese low-nickel austenitic steels has been assembled and published, additional data are required before these steels can be accepted by industry for many purposes in which severe corrosive attack is involved.

Steel producers in the U.S.A. have already done a certain amount of co-operative work on this subject, and the primary purpose of this paper, which comes from the laboratories of Union Carbide and Chemicals Company, is 'to collate the data obtained up to the present in various chemical processes, on the corrosion-resistance of the chromium-manganese-nickel steels as compared with that of the 18-8 chromium-nickel steels'. Both experimental and standard compositions of the low-nickel steels are represented, and the information given is based on the authors' own extensive tests, together with information received from other industrial and laboratory sources. The results include study of the susceptibility of the respective steels to intergranular corrosion and of behaviour in the sensitized and unsensitized conditions. Information on the influence of fabricating processes on behaviour in corrosive environments is also included.

The particulars given in the text are highly detailed, and not susceptible to individual abstracting, but the scope of the conditions considered and the reaction of the steels in such environments, are broadly indicated below.

*Conditions for which test results are given:*

Storage of weak (30 per cent.) acetic acid.
Conditions present in an acetic-acid/acetic-anhydride distillation process.
„ „ in preparation of cyclic diamine at high temperature and low pressure.
„ „ in preparation of an organo nitrile.
Corrosion in organic aldehydes.
„ „ organic acids.
„ „ esters and esterification reactions.
„ „ chlorides.
„ „ sulphates.
„ „ organo-nitrogen compounds.
„ „ other miscellaneous corrodents (including phosphoric acid, and halogens, alcohols and phenol).

Tabular data, with comments, demonstrate the relative resistance of the '200' and '300' steels in the above conditions.

The all-over conclusion drawn is that in many of the chemical environments considered the chromium-manganese-nickel steels offer resistance equal to that of the higher-nickel chromium-nickel standard steels of the A.I.S.I. 300 series. For example, they may probably be used with safety for organic-acid exposures at moderate temperatures, and in handling aldehydes, phenol and many organic products at ambient temperatures: in cases where organo-nitrogen compounds or conventional amines are the major corrosive constituents encountered, the chromium-manganese-nickel steels may offer some advantages.

Environments in which the lower-nickel steels do not appear to be so resistant to corrosion as the 18-8 chromium-nickel types are organic-acid/anhydride solutions at elevated temperatures and certain esterification reactions. In the presence of halogen compounds, and possibly in sulphate media also, they are inferior to the chromium-nickel steels.

The chromium-manganese-nickel steels, in the sensitized condition, appear to be more susceptible than the 18-8 types to intergranular corrosion in certain media, and, since high-manganese, low-nickel steels are not readily amenable to stabilization by addition elements, the carbon content of the steels,

and this susceptibility to intergranular attack are features which call for further detailed investigation in relation to the use of such steels in severely corrosive conditions.

### Chloride Stress-Corrosion Cracking of Austenitic Steels: Hydrochloric-Acid Cleaning Solutions

J. P. ENGLE, G. L. FLOYD and R. B. ROSENE: 'Chloride Stress-Corrosion Cracking of the Austenitic Stainless Steels.'

*N.A.C.E. Tech. Committee Report, Publn.* 59-5. *Corrosion*, 1959, vol. 15, Feb., pp. 69t-72t.

In spite of the wealth of information, both theoretical and practical, which has become available on the austenitic stainless steels, there are, from time to time, cases of incorrect use or treatment. This report is concerned with the importance of correct maintenance technique, with particular reference to cleaning of stainless-steel equipment by the use of chemical solvents.

Hydrochloric acid has many advantages for this purpose and is widely used in industry, but in view of the known effect of chlorides in producing stress-corrosion cracking of austenitic steels, the National Association of Corrosion Engineers sponsored investigation of the conditions requisite for successful use of this method of cleaning without risk of corrosion attack. The materials used in the tests were straight 18-8 chromium-nickel (A.I.S.I. Type 304) and niobium-stabilized 18-8 (Type 347).

The experimental procedure used, and the conclusions drawn from the tests, are outlined below.

Material was cut from ⅛-in. (3-mm.) sheet of the steels, longitudinally to the direction of rolling: the specimens were formed into arc-shaped horseshoe specimens and were annealed in an inert atmosphere. They were then stressed to 75 per cent. of the yield-strength value, by tightening a stainless-steel bolt passing through the ends of the specimens. (A typical assembly is illustrated.) Test specimens of similar type were prepared from cold-rolled material, to simulate fabricated material of higher strength and lower ductility. A third series comprised similar specimens of the Type 304 steel in the sensitized condition produced by heating the steel, before preparation of the specimens, at 1100°F. (595°C.) for four hours. These specimens were designed to simulate material in a condition resulting from welding of unstabilized austenitic steel.

All the statically stressed horseshoe specimens were exposed, for six hours each day, in inhibited 7·5 wt. per cent. hydrochloric-acid solutions at 150°F. (65·5°C.), to a total period of 120 hours. The conditions were thus representative of a number of repeated cleanings of material in the annealed, the cold-rolled, and the sensitized conditions. On completion of exposure, the specimens were subjected to a 180° bend test (according to A.S.T.M. A 240-49) and were metallographically examined.

Provision was also made for considering cases in which, following a chemical-cleaning operation, the solvent is not completely removed by the subsequent flushing operation. During the neutralizing by weak alkaline solution small amounts of sodium chloride may form, and remain on parts of the work. To determine the effect of such residual chlorides, static tests were made with stressed specimens in distilled water containing 50, 100 and 500 p.p.m. sodium chloride, at 400°F. (205°C.). One specimen in each test vessel was immersed in the test solution, and a counterpart specimen was suspended in the vapour and intermittently wetted once each hour by inversion of the vessel. (Equipment is illustrated.)

Typical photomicrographs show the effects produced on the steel specimens in the various conditions, and the effects of varying time and conditions of exposure are reported.

The observations made lead to the conclusion that the active-passive characteristics of the steels have a significance which has probably not hitherto been duly appreciated. In hydrochloric-acid solutions the passive film on stainless steels is removed, even when a highly efficient inhibitor is present, and the exposure test results reported, supported by measurements of the electrode potentials of the steels in various conditions, indicate that when the steels are in the active condition they are not subject to chloride stress-corrosion cracking. Hydrochloric-acid solutions, as used for maintenance-cleaning purposes, will not produce cracking if the metal surface is in an entirely activated condition. Under such conditions the extent of metal loss depends upon the efficiency of the inhibitor; it should be only low and quite uniform.

Flushing after acid cleaning usually involves a water rinse which may be followed by a flushing in an alkaline solution. Due to oxygen in the wash water, the potential of the metal changes in a direction indicating that passivity is restored. (The introduction of air between the stages has the same effect.) Units thus passivated, on which traces of sodium chloride may be present, e.g., in crevices, are frequently returned to the chemical unit in that condition, and the tests in distilled water containing sodium chloride (see above) indicated that in steel in such condition cracking readily occurs. A brief note of warning is given on dangerous conditions which may arise due to leaching of chloride onto metal surfaces, e.g., from insulators. A typical example of such damage is illustrated. (In this connexion, see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 2, p. 59.) In sensitized material time to onset of cracking is very short.

Metallurgical examination showed that the corrosion product occurred in 'scabs' and that cracking originated in steep-walled pits. The annealed and the cold-rolled specimens showed typical *trans*granular stress-corrosion cracking; in the specimens prepared from sensitized material the cracking was of the regular *inter*crystalline nature characteristic of deterioration of sensitized austenitic steels.

The results thus indicate that, with correct procedure,

cleaning of austenitic steel components in inhibited hydrochloric-acid solutions does not result in stress-corrosion cracking.

**Resistance of Nickel-bearing Materials to Nitric-Acid/Hydrofluoric-Acid Solutions containing Reducing Agents**

M. L. HOLZWORTH: 'Corrosion by Solutions Containing $HNO_3$, HF, and Reducing Agents.'
*U.S. Atomic Energy Commission, Report DP*-284, May 1958; 24 pp.

The work described originated in the development of a chemical process which involved handling a mixture of nitric and hydrofluoric acids containing several strong reducing agents. Lack of pertinent information on which to base selection of a suitable material of construction led to initiation of the investigation now reported. The aim of the work was (1) to find a material with the necessary corrosion-resistance, or (2) to determine a complexing agent or an inhibitor which would permit use of stainless-steel equipment. Corrosion rates of about 25 mils/year were considered acceptable.

The two main materials studied were a niobium-containing and an extra-low-carbon grade of chromium-nickel stainless steel (A.I.S.I. Types 309-Nb and 304L). Specimens were exposed, for five 48-hour periods, to a solution of the following basis composition: nitric acid 1·92, hydrofluoric acid 1·08, hydroxylamine nitrate 0·08, sulphamic acid 0·11, ascorbic acid 0·02, mole per litre. The solution was changed, and the specimens were weighed, after each 48-hour period. In some experiments the effects of varying the concentration of the individual basis constituents was studied, and in others the inhibitive effects of additions of aluminium or of reducible cations such as ferric, cupric or silver ions were determined.

The results show that the corrosion rate of the stainless steels in the nitric-acid/hydrofluoric-acid mixture was considerably increased by addition of hydroxylamine nitrate or sulphamic acid: addition of ascorbic acid had no effect in this respect. Introduction of either aluminium or silver ions was, however, found to decrease corrosion of both steels to less than 20 mils/year, and in the case of the niobium-containing steel addition of very small concentrations of either cupric or ferric ions lowered the rate of corrosion to less than 5 mils/year.

Of the other materials tested in the multi-component solution, silver, 'Hastelloy C' and 'Monel' corroded at rates below 5 mils/year, and of these, 'Hastelloy C' is considered particularly suitable for use in the application envisaged. 'Hastelloy B', 'Haynes 25', 'Carpenter 20' and 'Ni-O-Nel' showed rates ranging from 7 to 26 mils/year. 'Inconel', and titanium, like the several 18-8-type stainless steels tested, had rates of from 165 to 2330 mils/year, and, without the use of complexing agents, could not be considered as materials of construction in the plant.

**Corrosion of Austenitic Steels in Acids: Evaluation by Three Methods of Test**

M. A. STREICHER: 'General and Intergranular Corrosion of Austenitic Stainless Steels in Acids. Effect of Cations in the Acids and the Influence of Heat-Treatment and Grain Size of the Steel.'
*Jnl. Electrochemical Soc.*, 1959, vol. 106, Mar., pp. 161–80.

The intensity of attack on stainless steels exposed to certain acid solutions may vary from light etching of grain boundaries to penetration so intense that it may lead to complete loss of mechanical strength or even to disintegration of the metal. Whether corrosion is predominantly by intergranular or by general attack depends on the difference in the rate of corrosion of the grain-boundary zones and of the grain faces, and this difference in rate is determined by the structure and composition of the grain boundaries and by the nature of the corroding medium.

This paper reports a detailed study of the type of intergranular attack produced by three acid solutions which have been used, or proposed for use, as evaluation tests for austenitic stainless steels: the boiling-nitric-acid (Huey) test, the ferric-sulphate/sulphuric-acid test and the copper-sulphate/sulphuric-acid test. Special attention was directed to the electrochemical action of the cations encountered in these solutions, either as inhibitors of general corrosion or as corrosion products, which may accelerate or retard intergranular attack. Among the factors of significance, in stainless steel, the effect of the following variables was investigated with regard to influence on intergranular corrosion: chromium carbides, sigma phase, and grain size. (In connexion with the study of these factors, the condition and structure of the steels used were determined by preliminary testing (1) by the oxalic-acid anodic-etching procedure (for determination of the presence of chromium carbide), and (2) by nitric-acid test (to ascertain the presence or absence of sigma phase).)

The steels tested were of the high-alloy '18-8' type (chromium 18–19, nickel 9–10, per cent.) with carbon 0·06 or 0·03 per cent., all conforming in composition to A.I.S.I. Type 304 or 304L; molybdenum-containing '18-8' within the limits of Type 316, and an extra-low-carbon version of the latter steel, Type 316L.

In each of the three series of tests full details are given of experimental technique and of the conclusions reached with regard to the influence of the variables studied. In the final section of the report the test techniques are used as the basis for comparison and interpretation of the types of intergranular attack produced by the various solutions. The results are summarized in terms of criteria which can be used to compare the applicability of these corroding acids for routine evaluation tests. From the large amount of data recorded, the following main conclusions are deduced:

Corrosion of stainless steels by nitric acid is determined largely by the crystallography of grain boundaries: there is preferential attack, even on annealed

steels. Increasing the rate of dissolution, either by an anodic current or by oxidizing cations, intensifies intergranular penetration. The same crystallographic factors which determine preferential corrosion also determine the precipitation of chromium carbides. Their presence leads to a very great intensification of intergranular attack, as does sigma phase, even when present only as an invisible, pre-precipitation constituent.

Oxidizing cations, such as $Cr^{+6}$, $Ce^{+4}$ and $Fe^{+3}$, increase the corrosion of stainless steels in nitric acid by cathodic depolarization, by shifting the open-circuit potential of cathodic areas towards more noble values and, probably, by depolarization of anodic areas.

The effect of surface finish on rate of corrosion is largely a function of the true (absolute) area produced by various finishes.

Ferric ions in ferric-sulphate/sulphuric-acid solution greatly inhibit general, or grain-face, corrosion, by anodic polarization. In place of the reduction of hydrogen ions and the evolution of hydrogen gas at cathodic areas, ferric ions are reduced, and the consumption of ferric ions is electrochemically equivalent to the weight of steel dissolved. On steels containing intergranularly precipitated chromium carbide, intergranular attack leads to dislodgement of grains and a readily detectable weight loss.

Data obtained in sulphuric-acid solutions containing ferric nitrate in place of ferric sulphate suggest that it may be possible to use this solution for development of a 24-hour evaluation test.

The action of cupric sulphate in the copper-sulphate/sulphuric-acid solution is similar to that of ferric ions, but intergranular attack on susceptible steels does not readily dislodge the grains, and it is therefore not possible to use weight loss for routine evaluation. In that solution intergranular attack is greatly accelerated by metallic copper immersed simultaneously with the stainless-steel specimen or in contact with it. This acceleration is a result of the formation of cuprous ions and of galvanic action by copper, which is the anode of this couple. The resulting galvanic current and the cuprous ions reduce anodic polarization most readily at grain boundaries containing chromium-carbide precipitate, and thereby greatly increase the rate of intergranular penetration. In the copper-sulphate/sulphuric-acid solution presence of sigma phase in the steel does not increase corrosion.

The influence of grain size depends on the method of measurement used (weight loss or change in electrical resistance) and the composition of the corroding solution.

Dissolution of stainless steels in all three acid solutions examined is predominantly under anodic control. The difference in grain-surface corrosion and in intergranular penetration at susceptible grain boundaries is attributed primarily to a lower susceptibility to polarization of the metal in such grain-boundary zones, rather than to any difference which may exist in the open-circuit potentials of grain surfaces and grain boundaries.

**Corrosion by Hydrogen Sulphide**

E. B. BACKENSTO and J. W. SJOBERG: 'Iso-corrosion Rate Curves for High-Temperature Hydrogen/Hydrogen Sulphide.'

*Corrosion*, 1959, vol. 15, Mar., pp. 125t-7t.

*N.A.C.E. Tech. Committee Report* 59-10.

The substance of this report was abstracted (from *Petroleum Refiner*) in *Nickel Bulletin*, 1959, vol. 32, No. 2, p. 57.

**Cathodic Protection in Chemical Plant**

NAT. ASSOCN. CORROSION ENGINEERS: 'Cathodic Protection of Process Equipment.'

*Corrosion*, 1959, vol. 15, Mar., pp. 123t-4t.

Cathodic protection of buried or submerged structures has recently received much attention, with particular reference to its use in preventing soil corrosion, or attack by fresh or brackish waters, or sea water, usually at ambient temperatures. Comparatively little attention has, however, been given to the application of the principle for the protection of chemical equipment. This report, prepared by the N.A.C.E. Task Group T-3G-3 on Cathodic Protection of Process Equipment, draws attention to the value of the method for this purpose. The subject is presented in the form of performance data obtained from typical installations in which cathodic protection has achieved reduction in corrosion attack. The case histories described include:

(1) a cooling coil of austenitic nickel-chromium-molybdenum steel (A.I.S.I. Type 316) working in a sodium-hypochlorite solution,

(2) lead pipe coils operating in tanks in which barium chloride was being treated,

(3) mild steel subjected (in experimental tests) to chemically pure 73 per cent. caustic containing 0·3 per cent. sodium chloride at 100°C.,

(4) copper and 'Hastelloy' components in reactor cells handling 10 per cent. hydrochloric acid at 60°C.,

(5) 18-8 chromium-nickel steel vessels processing a dilute sulphuric-acid/organic-acid mixture (pH 1·5) at 100°C.,

(6) copper steam coils in zinc chloride, and copper heating coils in ammonium chloride,

(7) nickel-lined tanks used in production of a high-purity crystalline salt: the process liquor was moderately alkaline and temperatures ranged up to 100°C.

Brief details are given, in each case, of the arrangements made to inhibit corrosion, and of the degree of protection obtained. The reports indicate the possible value of the method in chemical-engineering plant of various types.

### Design of Stainless-Steel Extrusions

R. E. PARET: 'Stainless-Steel Extrusions. Part I, Process Characteristics. Part II, Applications and Design Concepts.'

*Machine Design*, 1959, vol. 31, Jan. 8, pp. 114–7; Jan. 22, pp. 118–21.

Part I of the article 'introduces the designer to the extrusion process in terms of its applicability to stainless steel'; Part II 'shows where and how a stainless-steel extrusion can be designed into a product, how shapes can be modified for the extrusion process, and how the most advantageous shapes are determined'.

Extrusions in stainless steel offer the designer the following advantages: (1) freedom of section design, (2) reduction or elimination of machining operations, (3) production of integral shapes which could normally be produced only by joining two or more components, (4) economical production of small quantities of components when demand does not justify rolling, (5) production of shapes impossible to roll or not available in the grade of steel required, (6) ability to repeat an order as required by using the relevant extrusion die, (7) economies over comparable cast or forged components, (8) improved mechanical properties in parts subject in service to transverse loading. Illustrated notes on each of these eight factors are given in Part I of the article.

In Part II the author discusses the factors of primary interest to designers in relation to the extrusion of stainless steels: the design requirements for a good extrusion and the variety of shapes which may be obtained by the process. His outline of the fundamentals of design opens with a discussion of maximum and minimum sizes attainable in such extrusions and operational variables which are of significance in this respect. The influence of die design is illustrated by allusion to drawings of extrusions of thin section. Factors affecting tolerance control during extrusion are briefly reviewed, and reference is made to minimum radii for corners and fillets, and the tolerance attainable with angles. The article ends with notes on the production of stepped, tapered, and multiple extrusions, as indicating the potential of the extrusion process.

### Stainless-Steel Equipment in the Wet-Milling of Corn

R. BENES, F. J. HOLSINGER and R. E. PIERSON: 'Corrosion in the Corn Wet-Milling Industry.'

*Corrosion*, 1959, vol. 15, Mar., pp. 113t–16t.

The corn wet-milling industry, which, in the U.S.A., dates back to 1848, has, in the interim, assumed a major rôle in food and consumer-product manufacture. Among the important items associated with it are starch, corn syrup, and corn oil, products which are employed in many industries.

Corn processing involves the following basic operations: (1) milling and separation of the components; (2) production of starch and modified starches; (3) manufacture of sugar and syrups; (4) expulsion of oil, and refining; (5) production of by-products. The processes and equipment required in the respective stages vary widely, and the conditions obtaining, which involve handling many types of chemicals, give rise to corrosive attack of varying nature and severity. This article describes the processes involved at the various stages, with particular reference to the materials of construction which have proved suitable for the plant. Austenitic chromium-nickel stainless steel of the molybdenum-containing type is very extensively employed in several sections; in other applications the more complex higher-alloy austenitic steels are needed, and in a continuous converter used in the sugar- and syrup-producing plant particularly good service has been obtained from 'Hastelloy C' (nickel-molybdenum-chromium-iron alloy). In some sections of the plant non-metallic materials, particularly polyvinyl chloride (P.V.C.), are found to give the best service.

### Stainless Steel in Railway Engineering

'Denver Zephyrs.'

'International Railcars.'

*Diesel Railway Traction*, 1959, vol. 1, Mar., p. 128.

The two original stainless-steel 'Denver Zephyr' trains of the Burlington Lines in the U.S.A., which were introduced into the Chicago–Denver service in November 1936, have now covered an aggregate of 8,000,000 miles, or an average of 180,000 miles per train per year over the whole period.

Budd R.D.C. stainless-steel diesel-hydraulic railcars of the Canadian National Railways are now operating through services between Montreal and Boston, U.S.A.

### Nickel-Aluminium-Bronze Propellers: Production and Properties

See abstract on p. 148.

### Analytical Chemistry in the Atomic Energy Field

See abstract on p. 138.

### Determination of Cobalt and Nickel-containing Steels

See abstract on p. 151.

## ANALYSIS

### Analytical Chemistry in the Atomic Energy Field

See abstract on p. 138.

### Determination of Cobalt in Nickel and Nickel-containing Steels

See abstract on p. 151.

### Corrigendum

*Nickel Bulletin*, 1959, vol. 32, No. 1, p. 8.

K. SOMMER: 'Some Observations on the Form of Oil Pores in Nickel Electrodeposits', lines 2-3. For *Metall*, 1957, vol. 11, pp. 166–7 read *Metalloberfläche*, 1957, vol. 11, Nov., pp. 366–7.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

THE MOND NICKEL COMPANY LIMITED
THAMES HOUSE · MILLBANK · LONDON, S.W.1

PRINTED IN ENGLAND BY WIGHTMAN MOGRIDGE LTD.
WESTMINSTER, LONDON, S.W.1